

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE FORM PTO-1390 (Modified) (REV 11-2000)		ATTORNEY'S DOCKET NUMBER <b>220952US0PCT</b>
<b>TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371</b>		U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR <b>10/089064</b>
INTERNATIONAL APPLICATION NO. <b>PCT/EP00/09746</b>	INTERNATIONAL FILING DATE <b>5 October 2000</b>	PRIORITY DATE CLAIMED <b>6 October 1999</b>
TITLE OF INVENTION <b>PREPARATION OF POLYISOBUTENYLPHENOL-CONTAINING MANNICH ADDUCTS</b>		
APPLICANT(S) FOR DO/EO/US <b>Arno LANGE et al.</b>		
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:		
<ol style="list-style-type: none"> <li>1. <input checked="" type="checkbox"/> This is a <b>FIRST</b> submission of items concerning a filing under 35 U.S.C. 371.</li> <li>2. <input type="checkbox"/> This is a <b>SECOND</b> or <b>SUBSEQUENT</b> submission of items concerning a filing under 35 U.S.C. 371.</li> <li>3. <input checked="" type="checkbox"/> This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (24) indicated below.</li> <li>4. <input checked="" type="checkbox"/> The US has been elected by the expiration of 19 months from the priority date (Article 31).</li> <li>5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371 (c) (2))             <ol style="list-style-type: none"> <li>a. <input type="checkbox"/> is attached hereto (required only if not communicated by the International Bureau).</li> <li>b. <input checked="" type="checkbox"/> has been communicated by the International Bureau.</li> <li>c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US).</li> </ol> </li> <li>6. <input checked="" type="checkbox"/> An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).             <ol style="list-style-type: none"> <li>a. <input checked="" type="checkbox"/> is attached hereto.</li> <li>b. <input type="checkbox"/> has been previously submitted under 35 U.S.C. 154(d)(4).</li> </ol> </li> <li>7. <input checked="" type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))             <ol style="list-style-type: none"> <li>a. <input type="checkbox"/> are attached hereto (required only if not communicated by the International Bureau).</li> <li>b. <input type="checkbox"/> have been communicated by the International Bureau.</li> <li>c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired.</li> <li>d. <input checked="" type="checkbox"/> have not been made and will not be made.</li> </ol> </li> <li>8. <input type="checkbox"/> An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).</li> <li>9. <input checked="" type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).</li> <li>10. <input checked="" type="checkbox"/> An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).</li> <li>11. <input type="checkbox"/> A copy of the International Preliminary Examination Report (PCT/IPEA/409).</li> <li>12. <input checked="" type="checkbox"/> A copy of the International Search Report (PCT/ISA/210).</li> </ol>		
Items 13 to 20 below concern document(s) or information included:		
<ol style="list-style-type: none"> <li>13. <input checked="" type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98.</li> <li>14. <input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.</li> <li>15. <input checked="" type="checkbox"/> A <b>FIRST</b> preliminary amendment.</li> <li>16. <input type="checkbox"/> A <b>SECOND</b> or <b>SUBSEQUENT</b> preliminary amendment.</li> <li>17. <input type="checkbox"/> A substitute specification.</li> <li>18. <input type="checkbox"/> A change of power of attorney and/or address letter.</li> <li>19. <input type="checkbox"/> A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.</li> <li>20. <input type="checkbox"/> A second copy of the published international application under 35 U.S.C. 154(d)(4).</li> <li>21. <input type="checkbox"/> A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).</li> <li>22. <input type="checkbox"/> Certificate of Mailing by Express Mail</li> <li>23. <input checked="" type="checkbox"/> Other items or information:</li> </ol>		
<b>Notice of Priority/ Form PTO-1449</b> <b>PCT/IB/304/ PCT/IB/308</b> <b>Amended Sheets (pages 41, 42, 43, 43a)</b>		

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR <b>107089064</b>	INTERNATIONAL APPLICATION NO. <b>PCT/EP00/09746</b>	ATTORNEY'S DOCKET NUMBER <b>220952US0PCT</b>																
24. The following fees are submitted:		<b>CALCULATIONS PTO USE ONLY</b>																
<b>BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :</b>																		
<input type="checkbox"/> Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO ..... <b>\$1040.00</b> <input checked="" type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO ..... <b>\$890.00</b> <input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO ..... <b>\$740.00</b> <input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) ..... <b>\$710.00</b> <input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) ..... <b>\$100.00</b>																		
<b>ENTER APPROPRIATE BASIC FEE AMOUNT =</b>		<b>\$890.00</b>																
Surcharge of <b>\$130.00</b> for furnishing the oath or declaration later than months from the earliest claimed priority date (37 CFR 1.492 (e)).		<input type="checkbox"/> 20 <input type="checkbox"/> 30 <b>\$0.00</b>																
<table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 25%;">CLAIMS</th> <th style="width: 25%;">NUMBER FILED</th> <th style="width: 25%;">NUMBER EXTRA</th> <th style="width: 25%;">RATE</th> </tr> </thead> <tbody> <tr> <td>Total claims</td> <td>17 - 20 =</td> <td>0</td> <td>x \$18.00    <b>\$0.00</b></td> </tr> <tr> <td>Independent claims</td> <td>2 - 3 =</td> <td>0</td> <td>x \$84.00    <b>\$0.00</b></td> </tr> <tr> <td colspan="2">Multiple Dependent Claims (check if applicable).</td> <td style="text-align: center;"><input type="checkbox"/></td> <td style="text-align: center;"><b>\$0.00</b></td> </tr> </tbody> </table>		CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	Total claims	17 - 20 =	0	x \$18.00 <b>\$0.00</b>	Independent claims	2 - 3 =	0	x \$84.00 <b>\$0.00</b>	Multiple Dependent Claims (check if applicable).		<input type="checkbox"/>	<b>\$0.00</b>	
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<b>TOTAL OF ABOVE CALCULATIONS =</b>		<b>\$890.00</b>																
<input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27). The fees indicated above are reduced by 1/2.		<b>\$0.00</b>																
<b>SUBTOTAL =</b>		<b>\$890.00</b>																
Processing fee of <b>\$130.00</b> for furnishing the English translation later than months from the earliest claimed priority date (37 CFR 1.492 (f)).		<input type="checkbox"/> 20 <input type="checkbox"/> 30    + <b>\$0.00</b>																
<b>TOTAL NATIONAL FEE =</b>		<b>\$890.00</b>																
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable).		<input type="checkbox"/> <b>\$0.00</b>																
<b>TOTAL FEES ENCLOSED =</b>		<b>\$890.00</b>																
		<b>Amount to be: refunded</b> <b>\$</b> <b>charged</b> <b>\$</b>																
a. <input checked="" type="checkbox"/> A check in the amount of <b>\$890.00</b> to cover the above fees is enclosed. b. <input type="checkbox"/> Please charge my Deposit Account No. _____ in the amount of _____ to cover the above fees. A duplicate copy of this sheet is enclosed. c. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. <b>15-0030</b> A duplicate copy of this sheet is enclosed. d. <input type="checkbox"/> Fees are to be charged to a credit card. <b>WARNING: Information on this form may become public. Credit card information should not be included on this form.</b> Provide credit card information and authorization on PTO-2038.																		
NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.																		
SEND ALL CORRESPONDENCE TO:																		
 <b>22850</b>																		
 <b>SIGNATURE</b> <b>Novelle E. Obrien Beaumont</b> <b>NAME</b> <b>Registration Number 30,995</b> <b>24,618</b> <b>REGISTRATION NUMBER</b> <b>April 5, 2002</b> <b>DATE</b>																		

220952US-0PCT

IN THE UNITED STATES PATENT & TRADEMARK OFFICE

IN RE APPLICATION OF:

ARNO LANGE ET AL : ATTN: APPLICATION DIVISION

SERIAL NO: NEW U.S. PCT APPLN :  
(Based on PCT NO/EP00/09746)

FILED: HEREWITH : EXAMINER:

FOR: PREPARATION OF  
POLYISOBUTENYLPHENOL-CONTAINING  
MANNICH ADDUCTS

PRELIMINARY AMENDMENT

ASSISTANT COMMISSIONER FOR PATENTS  
WASHINGTON, D.C. 20231

SIR:

Prior to examination on the merits, please amend the above-identified application as follows:

IN THE TITLE

Please delete the title and replace with the following title:

--METHOD FOR PRODUCING MANNICH ADDUCTS THAT CONTAIN  
POLYISOBUTYLENE PHENOL--

IN THE CLAIMS

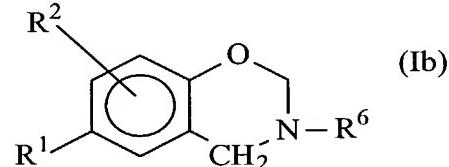
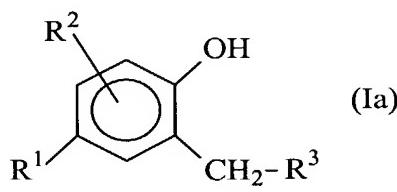
Please cancel Claims 11 and 15.

Please amend the claims as shown on the marked-up copy following this amendment to read as follows:

2. (Amended) The process as claimed in claim 1, wherein the amine is 3-(dimethylamino)-n-propylamine, di[3-(dimethylamino)-n-propyl]amine, dimethylamine, diethylamine, di-n-propylamine or morpholine.

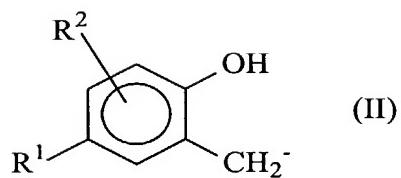
3. (Amended) The process as claimed in claim 1, wherein, in step c), the adduct is an aminal of formaldehyde with a secondary amine selected from the group consisting of di-C<sub>1</sub>-C<sub>8</sub>-alkylamines whose alkyl groups may be substituted by an N(C<sub>1</sub>-C<sub>4</sub>-alkyl)<sub>2</sub> group and cyclic amines which have 4 to 6 carbon atoms and whose cyclic structure may be interrupted by O and/or N-C<sub>1</sub>-C<sub>4</sub>-alkyl.

4. (Amended) The process as claimed in Claim 1, wherein an adduct mixture is obtained which comprises at least 40 mol% of compounds of the formula Ia and/or Ib,



where

- R<sup>1</sup> is a terminally bonded polyisobut enyl radical,
- R<sup>2</sup> is H, C<sub>1</sub>- to C<sub>20</sub>-alkyl, C<sub>1</sub>- to C<sub>20</sub>-alkoxy, hydroxyl, a polyalkylenyl radical or CH<sub>2</sub>NR<sup>4</sup>R<sup>5</sup>, where R<sup>4</sup> and R<sup>5</sup> have the meanings stated below, and
- R<sup>3</sup> is NR<sup>4</sup>R<sup>5</sup>, where R<sup>4</sup> and R<sup>5</sup>, independently of one another, are H, C<sub>1</sub>- to C<sub>20</sub>-alkyl, C<sub>3</sub>- to C<sub>8</sub>-cycloalkyl and C<sub>1</sub>- to C<sub>20</sub>-alkoxy radicals which may be interrupted and/or substituted by N and O heteroatoms, and phenol radicals of the formula II



where  $R^1$  and  $R^2$  are as defined above;

with the proviso that  $R^4$  and  $R^5$  are not simultaneously H or phenol radicals of the formula II; or  $R^4$  and  $R^5$ , together with the N atom to which they are bonded, form a 5-, 6- or 7-membered cyclic structure which has one or two N and O heteroatoms and may be substituted by one, two or three  $C_1$ - to  $C_6$ -alkyl radicals; and

$R^6$  is a radical  $R^4$  or  $R^5$  other than H.

5. (Amended) The process as claimed in Claim 1, wherein a Mannich adduct having a polydispersity of from 1.1 to 3.5 is obtained.

6. (Amended) The process as claimed in Claim 1, wherein, in step c), the reaction product from a) is reacted with at least one adduct of amine and formaldehyde, an oligomer of formaldehyde, a polymer of formaldehyde or a formaldehyde equivalent by reacting the two reactants for at least 15 minutes at above +15°C to prepare the Mannich adduct.

7. (Amended) The process as claimed in Claim 1, wherein the reaction mixture from b) or c) is fractionated by column chromatography over an acidic stationary phase by multistage elution with

- at least one hydrocarbon and then
- at least one basic alcohol/water mixture.

8. (Amended) The process as claimed in claim 7, wherein the basic alcohol/water mixture is a mixture of

- a) from 75 to 99.5% by weight of at least one C<sub>2</sub>- to C<sub>4</sub>-alcohol,
- b) from 0.4 to 24.4% by weight of water, and
- c) from 0.1 to 15% by weight of at least one amine which is volatile at room temperature.

9. (Amended) The process as claimed in Claim 1, wherein an adduct mixture obtained includes from 0 to 20 mol% of polyisobutarylphenols from reaction step a) which are not reacted further.

10. (Amended) A Mannich adduct obtained by

- a) alkylation of a phenol with polyisobutene having more than 70 mol % of vinylidene double bonds and a number average molecular weight of from 300 to 3000 at below about 50°C in the presence of an alkylation catalyst;
- b) reaction of the reaction product from a) with formaldehyde, an oligomer or a polymer of formaldehyde and at least one amine which has at least one secondary amino function and no primary amino function.

12. (Amended) An additive concentrate containing, in addition to conventional additive components, at least one Mannich adduct as claimed in claim 10 in amounts of from 0.1 to 99.9% by weight.

Please add the following new claims:

16. (New) A method of preparing a detergetized fuel or lubricant comprising mixing the Mannich adduct of Claim 10 with a fuel or a lubricant.

17. (New) A method of preparing a detergetized gasoline or diesel fuel comprising mixing the Mannich adduct of Claim 10 with a gasoline or a diesel fuel.

18. (New) The process as claimed in Claim 1, wherein an adduct mixture obtained includes from 1-15 mol% of polyisobut enylphenols from reaction step a) which are not reacted further.

19. (New) An additive concentrate containing, in addition to conventional additive components, at least one Mannich adduct as claimed in Claim 10 in amounts of from 0.5-80% by weight.

REMARKS

Claims 1-10, 12-14 and 16-19 are active in the present application. Claims 11 and 15 have been cancelled. Claims 16-19 are new claims. Support for the new claims is found in the original claims. No new matter is believed to have been added by this amendment. An action on the merits and allowance of claims is solicited.

Respectfully submitted,

OBLON, SPIVAK, McCLELLAND,  
MAIER & NEUSTADT, P.C.



Norman F. Oblon  
Attorney of Record  
Registration No. 24,618

Stefan U. Koschmieder, Ph.D.  
Registration No. 50,238



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**Marked-Up Copy**  
Serial No: \_\_\_\_\_  
Amendment Filed on:  
4-5-2002

**IN THE TITLE**

Please delete the title and replace with the following title.

[PREPARATION OF POLYISOBUTENYLPHENOL-CONTAINING MANNICH ADDUCTS]

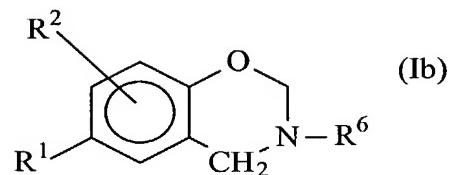
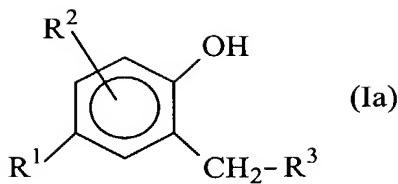
--METHOD FOR PRODUCING MANNICH ADDUCTS THAT CONTAIN POLYISOBUTYLENE PHENOL--

**IN THE CLAIMS**

2. (Amended) [A] The process as claimed in claim 1, wherein the amine [used] is 3-(dimethylamino)-n-propylamine, di[3-(dimethylamino)-n-propyl]amine, dimethylamine, diethylamine, di-n-propylamine or morpholine.

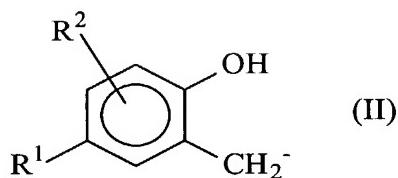
3. (Amended) [A] The process as claimed in claim 1, wherein, in step c), the adduct [used] is an aminal of formaldehyde with a secondary amine[,] selected from the group consisting of di-C<sub>1</sub>-C<sub>8</sub>-alkylamines whose alkyl groups may be substituted by an N(C<sub>1</sub>-C<sub>4</sub>-alkyl)<sub>2</sub> group[,] and cyclic amines[,] which have 4 to 6 carbon atoms and whose cyclic structure may be interrupted by O and/or N-C<sub>1</sub>-C<sub>4</sub>-alkyl.

4. (Amended) [A] The process as claimed in [any of the preceding claims] Claim 1, wherein an adduct mixture is obtained which comprises at least 40 mol% of compounds of the formula Ia and/or Ib,



where

- R<sup>1</sup> is a terminally bonded polyisobut enyl radical,
- R<sup>2</sup> is H, C<sub>1</sub>- to C<sub>20</sub>-alkyl, C<sub>1</sub>- to C<sub>20</sub>-alkoxy, hydroxyl, a polyalkylenyl radical or CH<sub>2</sub>NR<sup>4</sup>R<sup>5</sup>, where R<sup>4</sup> and R<sup>5</sup> have the meanings stated below, and
- R<sup>3</sup> is NR<sup>4</sup>R<sup>5</sup>, where R<sup>4</sup> and R<sup>5</sup>, independently of one another, are [selected from] H, C<sub>1</sub>- to C<sub>20</sub>-alkyl, C<sub>3</sub>- to C<sub>8</sub>-cycloalkyl and C<sub>1</sub>- to C<sub>20</sub>-alkoxy radicals which may be interrupted and/or substituted by [heteroatoms selected from] N and O heteroatoms, and phenol radicals of the formula II



where R<sup>1</sup> and R<sup>2</sup> are as defined above;

with the proviso that R<sup>4</sup> and R<sup>5</sup> are not simultaneously H or phenol radicals of the formula II; or R<sup>4</sup> and R<sup>5</sup>, together with the N atom to which they are bonded, form a 5-, 6- or 7-membered cyclic structure which has one or two [heteroatoms selected from] N and O heteroatoms and may be substituted by one, two or three C<sub>1</sub>- to C<sub>6</sub>-alkyl radicals; and

- R<sup>6</sup> is a radical R<sup>4</sup> or R<sup>5</sup> other than H.

5. (Amended) [A] The process as claimed in [any of the preceding claims] Claim 1, wherein a Mannich adduct having a polydispersity of from 1.1 to 3.5 is obtained.

6. (Amended) [A] The process as claimed in [any of the preceding claims] Claim 1, wherein, in step c), the reaction product from a) is reacted with [an adduct which is obtained from] at least one adduct of amine and formaldehyde, an oligomer of formaldehyde, a polymer of formaldehyde or a formaldehyde equivalent by reacting the two reactants for at least 15 minutes at above +15°C[ is used] to prepare the adduct.

7. (Amended) [A] The process as claimed in [any of claims 1 to 6] Claim 1, wherein the reaction mixture from b) or c) is fractionated by column chromatography over an acidic stationary phase by multistage elution with

- at least one hydrocarbon and then
- at least one basic alcohol/water mixture.

8. (Amended) [A] The process as claimed in claim 7, wherein the basic alcohol/water mixture [used] is a mixture of

- a) from 75 to 99.5% by weight of at least one C<sub>2</sub>- to C<sub>4</sub>-alcohol,
- b) from 0.4 to 24.4% by weight of water, and
- c) from 0.1 to 15% by weight of at least one amine which is volatile at room temperature.

9. (Amended) [A] The process as claimed in [any of the preceding claims] Claim 1, wherein [the] an adduct mixture obtained includes from 0 to 20 [, preferably 1 to 15,] mol% of polyisobutetylphenols from reaction step a) which are not reacted further.

10. (Amended) A Mannich adduct [obtainable] obtained by

- a) alkylation of a phenol with polyisobutene having more than 70 mol % of vinylidene double bonds and a number average molecular weight of from 300 to 3000 at below about 50°C in the presence of an alkylation catalyst;
- b) reaction of the reaction product from a) with formaldehyde, an oligomer or a polymer of formaldehyde and at least one amine which has at least one secondary amino function and no primary amino function.

12. (Amended) An additive concentrate containing, in addition to conventional additive components, at least one Mannich adduct as claimed in claim 10 in amounts of from 0.1 to 99.9% by weight[, preferably 0.5 to 80% by weight].--

11. (Cancelled).

15. (Cancelled).

16. (New).

17. (New).

18. (New).

19. (New).

## Preparation of polyisobut enylphenol-containing Mannich adducts

5 The present invention relates to a process for the preparation of polyisobut enylphenol-containing Mannich adducts, the Mannich adducts obtainable by this process and the use of the Mannich adducts as detergent additives in fuel and lubricant compositions.

10

Carburetors and intake systems of gasoline engines, but also injection systems for metering fuel, are increasingly contaminated with impurities which are caused by dust particles from the air, uncombusted hydrocarbon residues from the

15 combustion chamber and the crank case vent gases passed into the carburetor.

These residues shift the air/fuel ratio during idling and in the lower part-load range so that the mixture becomes leaner and the

20 combustion more incomplete and hence the proportions of uncombusted or partially combusted hydrocarbons in the exhaust gas become greater. Increasing gasoline consumption is the result.

25 It is known that, in order to avoid these disadvantages, fuel additives for keeping valves and carburetors or injection systems of gasoline engines clean are used (cf. for example M. Rossenbeck in Katalysatoren, Tenside, Mineralöladditive, editors J. Falbe and U. Hasseroth, page 223, G. Thieme Verlag, Stuttgart 1978).

30

Outstanding fuel additives of this type are aminoalkylated polyalkenyl hydroaromatics, as generally obtainable by a Mannich reaction of amines and aldehydes with polyalkyl-substituted hydroxyaromatics. These Mannich adducts are obtained as a rule in 35 the form of complex mixtures of a plurality of amine-containing adducts having different cleaning activities and amine-free adducts generally having lower cleaning activities.

Such Mannich adducts generally have a good cleaning effect but 40 possess a number of disadvantages.

Owing to the complex composition of the mixtures, a dark color and an intense odor, which adversely affect customer acceptance, are often observed. More serious, however, is the fact that, 45 depending on composition, chain length of the polyalkylene moiety in the molecule, engine type and concentration in which the additive is used, such conventional Mannich adducts may cause

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sticking of the valves, which can lead to total engine failure. Sticking of the valves is understood as meaning complete loss of compression on one or more cylinders of the internal combustion engine if, owing to polymer deposits on the valve shaft, the 5 spring forces are no longer sufficient to close the valves properly.

Thus, a number of publications, for example GB-A-1,368,532, US-A-4,231,759, US-A-5,634,951 and US-A-5,725,612 describe fuel additives based on Mannich adducts, which are obtainable from polyolefin-substituted hydroxyaromatics. The Mannich adducts disclosed there are without exception those which are obtainable by alkylation of phenols with polyolefins having low reactivity and subsequent Mannich reaction. Such polyolefins having low reactivity are generally produced by polymerization of olefin mixtures and have a very nonuniform polymer backbone and a small proportion of terminal double bonds. The use of such polyolefins having low reactivity for the preparation of Mannich adducts leads to low yields in the alkylation step (less than 83%, cf. for example US-A-5,634,951), nonuniform product distribution and a moderate cleaning effect when used as a fuel additive.

In contrast, EP-A-0 831 141 describes improved detergents for hydrocarbon fuels, which are obtainable from a highly reactive 25 polyisobutene which has at least 70% olefinic double bonds of the vinylidene type, an aldehyde and ethylenediamine by a Mannich reaction with a polyisobutene-substituted phenol. The polyisobutenes used in the alkylation have an average molecular weight of 1000 and lead to polyisobutene-substituted phenols 30 which have a ratio of para to ortho substitution of about 3:1. Thus, Example 1 of this reference describes a polyisobutenyl-phenol having an ortho/para ratio of 1:3 which is prepared from highly reactive polyisobutene and phenol in a molar ratio of 1:2 in the presence of  $\text{BF}_3$  etherate. Here too, however, the Mannich 35 adducts thus obtained are present as complex mixtures having a broad distribution and comparatively low proportion of nitrogen, as is evident from the overall parameters of nitrogen content and base number, stated instead of the analytical data.

40 The fuel and lubricant additives known from the prior art and based on Mannich adducts contain as a rule < 50 mol% of nitrogen-containing compounds and have very broad molecular weight distributions. Consequently, these additives based on Mannich products were also incapable of eliminating the known problems, such as undesired color, unpleasant odor, and especially the problematic sticking of the valves. Moreover, a further increase in the efficiency of such fuel additives is

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desirable, on the other hand in order to keep pace with the increasing requirements arising from the progressive engine technology and, on the other hand, as far as possible to extend downward the concentration range for the additives in the fuel which is required for the desired effect.

It is an object of the present invention to provide a process for the preparation of Mannich products based on polyalkylenephensols and thereby obtainable Mannich adducts with polyalkylene phenols having improved properties.

We have surprisingly found that this object is achieved by a process in which specific polyisobutetyl-substituted phenols, which are obtained by alkylation of phenols with highly reactive polyisobutenes, are reacted either with formaldehyde or oligomers or polymers of formaldehyde in the presence of a secondary amine or with an adduct of at least one amine with formaldehyde, another formaldehyde source or a formaldehyde equivalent.

In particular, it is surprising that the Mannich adducts thus obtained exhibit substantially improved viscosity behavior, in particular at low temperatures, and an improved detergent effect without the common disadvantages of the prior art. The Mannich adducts thus obtained have a particularly high proportion of nitrogen-containing compounds and a comparatively narrow molecular weight distribution. Moreover, it was surprisingly found that, in contrast to the prior art, the cleaning effect of the Mannich adducts is only slightly dependent on the type and structure of the amine used. In addition, it was found that the Mannich adducts thus obtained can be particularly easily fractionated by column chromatography and hence made more uniform.

The present invention therefore relates to a process for the preparation of polyisobutetylphenol-containing Mannich adducts by

- a) alkylation of a phenol with highly reactive polyisobutene at below about 50°C in the presence of an alkylation catalyst;
- 40 b) reaction of the reaction product from a) with formaldehyde, an oligomer or a polymer of formaldehyde and at least one amine which has at least one secondary amino function and no primary amino function  
45 or

- c) reaction of the reaction product from a) with at least one adduct of at least one amine which has at least one secondary or primary amino function and formaldehyde, an oligomer of formaldehyde, a polymer of formaldehyde or a formaldehyde equivalent.

Suitable polyisobutenes are highly reactive polyisobutenes, which differ from the polyisobutenes having low reactivity through the content of terminally arranged ethylenic double bonds. Suitable 10 highly reactive polyisobutenes are, for example, polyisobutenes which have more than 70, in particular more than 80, especially more than 85, mol%, based on the polyisobutene macromolecules, of vinylidene double bonds. Particularly preferred polyisobutenes are those which have uniform polymer backbones. In particular, 15 those polymers which are composed of at least 85, preferably at least 90, particularly preferably at least 95, % by weight of isobutene units have uniform polymer backbones. Preferably, such highly reactive polyisobutenes have a number average molecular weight of from 200 to 20,000. Highly reactive polyisobutenes 20 which have an average molecular weight of from 300 to 3000, particularly preferably from 400 to 2500, very particularly preferably from 500 to 1500, for example a number average molecular weight of about 550, about 800, about 1000 or about 2300, are particularly suitable for the preparation of fuel 25 additives. Highly reactive polyisobutenes which have a number average molecular weight of from 2500 to 15,000, particularly preferably from 3000 to 12,500, very particularly preferably from 3000 to 10,000, for example a number average molecular weight of about 2300, about 5000 or about 8000, are particularly suitable 30 for the preparation of lubricant additives. Preferably, the highly reactive polyisobutenes moreover have a polydispersity of less than 3.0, in particular less than 1.9, particularly preferably less than 1.7 or less than 1.5. Polydispersity is understood as meaning the quotient of weight average molecular 35 weight  $M_W$  and number average molecular weight  $M_N$ .

Particularly suitable highly reactive polyisobutenes are, for example, the Glissopal® brands from BASF AG, in particular Glissopal 1000 ( $M_N = 1000$ ), Glissopal V 33 ( $M_N = 550$ ) and 40 Glissopal 2300 ( $M_N = 2300$ ) and mixtures thereof. Other number average molecular weights can be established in a manner known in principle by mixing polyisobutenes of different number average molecular weights or by extractive enrichment of polyisobutenes of specific molecular weight ranges. They are also obtainable by 45 direct synthesis.

A phenol is reacted (alkylated) with such a highly reactive polyisobutene in a first step (step a)). Aromatic hydroxy compounds, such as unsubstituted phenol and monosubstituted or disubstituted phenols, are very generally suitable for the reaction with highly reactive polyisobutenes. The aromatic hydroxy compound used for the alkylation is preferably selected from phenolic compounds with 1, 2 or 3 OH groups and with or without at least one further substituent. Particularly suitable substituted phenols are mono-ortho-substituted phenols. Suitable substituents are, for example, C<sub>1</sub>-C<sub>20</sub>-alkyl, C<sub>1</sub>-C<sub>20</sub>-alkoxy or a further polyalkylene radical, in particular polyalkylene radicals based on highly reactive polyisobutenes. Particularly suitable substituents are C<sub>1</sub>-C<sub>7</sub>-alkyl, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, tert-butyl and hexyl. Particularly suitable alkyl-substituted phenols are 2-methylphenol and 2-ethylphenol. Unsubstituted phenol is particularly preferred for the alkylation with polyisobutenes.

In the alkylation, the phenol is usually used in excess. For example, about a 1.1- to 6-fold, preferably 1.6- to 5-fold, excess, such as a 2-fold or a 4-fold excess, of the phenol is suitable. The crude product obtained is further reacted under b) or c), if required after purification.

In one embodiment of the present process, the phenol is used in excess in the preparation of the polyisobutenyphenol and, after the end of the reaction, the reaction mixture is freed from excess phenol by extraction with solvents, preferably polar solvents, such as water or C<sub>1</sub>-C<sub>6</sub>-alkanols or mixtures thereof, by stripping, i.e. by passing steam through or, if required, heating of gases, e.g. nitrogen, or by distillation.

The alkylation of the phenol is carried out at below about 50°C, preferably below 35°C, in particular below 25°C, in the presence of an alkylation catalyst. As a rule the alkylation is carried out at above -40°C, preferably above -30°C, in particular above -20°C. Temperatures from -10 to +30°C, in particular from -5 to +25°C, particularly preferably from 0 to +20°C, are particularly suitable for the alkylation.

Suitable alkylation catalysts are known to a person skilled in the art. For example, protic acids, such as sulfuric acid, phosphoric acid and organic sulfonic acids, e.g. trifluoromethanesulfonic acid, Lewis acids, such as aluminum trihalides, e.g. aluminum trichloride or aluminum tribromide, boron trihalides, e.g. boron trifluoride and boron trichloride, tin halides, e.g. tin tetrachloride, titanium halides, e.g.

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titanium tetrabromide and titanium tetrachloride, and iron halides, e.g. iron trichloride and iron tribromide, are suitable. Adducts of boron trihalides, in particular boron trifluoride, with electron donors such as alcohols, in particular

- 5 C<sub>1</sub>-C<sub>6</sub>-alkanols or phenols, or ethers are preferred. Boron trifluoride etherate is particularly preferred.

The alkylation is preferably carried out in a liquid medium. For this purpose, the phenol is preferably dissolved in one of the reactants and/or in a solvent, if necessary with heating. In a preferred embodiment, the alkylation is preferably carried out by first melting the phenol or the substituted phenol by supplying heat and then adding a suitable solvent and/or the alkylation catalyst, in particular the boron trihalide adduct. The liquid mixture is then brought to a suitable reaction temperature. In a further preferred embodiment the phenol is first melted and the polyisobutene and, if required, suitable solvent are added. The liquid mixture thus obtained can be brought to a suitable reaction temperature and the alkylation catalyst can then be added.

Suitable solvents for carrying out this reaction are, for example, hydrocarbons, preferably pentane, hexane and heptane, in particular hexane, hydrocarbon mixtures, e.g. petroleum naphthas having boiling ranges from 35 to 100°C, dialkyl ethers, in particular diethyl ether, and halogenated hydrocarbons, such as dichloromethane or trichloromethane, and mixtures of the abovementioned solvents.

- 30 The reaction is preferably initiated by adding the catalyst or one of the two reactants, phenol or polyisobutene. The addition of the component initiating the reaction is preferably effected over a period of from 5 to 300, preferably from 10 to 200, in particular from 15 to 180, minutes, the temperature of the

35 reaction mixture advantageously not exceeding the abovementioned temperature ranges. After the end of the addition, the reaction mixture is allowed to continue reacting for preferably from 30 minutes to 24 hours, in particular from 60 minutes to 16 hours, at below 30°C. The reaction conditions are preferably chosen so

40 that at least 85%, in particular at least 90%, particularly preferably at least 95%, of the polyisobutenylphenol form. The polyisobutenyl-substituted phenols thus obtained preferably comprise (where the aromatic hydroxy compound used as the starting material allows) more than 85%, in particular more than

45 90%, and particularly preferably more than 95%, of isomers whose

**polyisobut enyl radical is para to the hydroxyl group of the phenol.**

Preferably, the alkylation product used for the subsequent reaction in steps b) and c) includes little if any unconverted phenol.

When the aromatic hydroxy compound used for the alkylation in step a) allows multiple alkylations, the reaction is preferably carried out in such a way that the polyisobut enylphenols obtained include little if any product more than monoalkylated by the polyisobutene. In fact, the alkylation products used for the subsequent reaction in steps b) or c) include not more than 20 mol%, preferably not more than 10 mol%, especially not more than 5 mol%, based on the total amount of alkylation products, of more than monoalkylated phenols.

The reaction product obtained under a) can be converted into the novel, advantageous Mannich adduct in two different ways. On the one hand, the reaction product obtained under a) can be reacted under b) with formaldehyde, an oligomer and/or a polymer of formaldehyde (also referred to below as a formaldehyde source) and at least one amine which has at least one secondary and no primary amino function.

25 On the other hand, the reaction product obtained under a) can be reacted under c) with at least one adduct of at least one amine which has at least one secondary or primary amino function and formaldehyde, an oligomer or a polymer of formaldehyde (these are  
30 also referred to below as formaldehyde sources) or a formaldehyde equivalent. In the context of the invention, formaldehyde equivalents are methylene components which are capable of reacting with amines to give imines or aminals, such as dihalomethane, in particular dichloro- and dibromomethane, and  
35 dialkoxymethane, in particular dimethoxymethane and diethoxymethane.

These reactions are referred to as a rule as Mannich or Mannich-analogous reactions.

40 Formaldehyde sources suitable for the reaction according to b) or  
c) are formalin solutions, formaldehyde oligomers, e.g. trioxane,  
and polymers of formaldehyde, such as paraformaldehyde.  
Paraformaldehyde is preferably used. Formalin solution is  
45 particularly easy to handle. Of course, gaseous formaldehyde may  
also be used.

Suitable amines for the reaction according to b) have at least one secondary amino function and, if required, one or more tertiary amino functions. What is important is that the amines reacted according to b) have no primary amino function, since otherwise larger amounts of undesired oligomerization products may occur. In the context of this invention, primary amino functions are amino functions of the formula  $\text{HNR}^4\text{R}^5$ , where one of the radicals  $\text{R}^4$  or  $\text{R}^5$  is hydrogen and the other radical is chosen from substituents other than hydrogen. In the context of this invention, secondary amino functions are amino functions of the formula  $\text{HNR}^4\text{R}^5$ , where  $\text{R}^4$  and  $\text{R}^5$  are chosen from substituents other than hydrogen. If amines which have no primary amino function and only one, two or three secondary amino functions, preferably only one secondary amino function, are used for the reaction according to b) nitrogen-containing Mannich adducts can be prepared with high selectivity, substantially independently of the order of combination of the reactants, the product spectrum being easily controllable by means of the chosen stoichiometry of the components polyisobut enylphenol, amine and formaldehyde source.

Suitable amines for the reaction according to c) have at least one primary or secondary amino function. Amines suitable for the reaction according to c) may have one or more primary amino functions and/or one or more secondary amino functions and moreover further tertiary amino functions. What is important for the preparation of the novel Mannich adducts by this variant is that an adduct is formed from at least one amine and a formaldehyde source or a formaldehyde equivalent in the absence of the polyisobut enylphenol, and this adduct is only then reacted with the polyisobut enylphenol. Starting from amines which have one or more primary amino groups, this process too leads to the formation of the novel, advantageous Mannich adducts having a high proportion of nitrogen-containing compounds and mixtures having a molecular weight distribution substantially narrower than the prior art.

Secondary amines reacted under b) lead, substantially independently of the order of combination of the reactants, to the selective formation of comparatively uniform amine-containing Mannich adducts. This is presumably due to the fact that the Mannich adducts formed starting from secondary amines are no longer capable of reacting with further formaldehyde and/or polyisobut enylphenol to give higher adducts (e.g. oligomers and polymers). Independently of the order of combination of the reactants, as described under c), the generally higher reactivity of secondary amines with respect to nucleophiles may lead to prior formation of adducts of formaldehyde and amine(s). This

would be in agreement with the good selectivity also found for the novel process carried out according to c).

In the amines of the formula  $\text{HNR}^4\text{R}^5$ ,  $\text{R}^4$  and  $\text{R}^5$  are preferably chosen from hydrogen and  $\text{C}_1$ - to  $\text{C}_{20}$ -alkyl,  $\text{C}_3$ - to  $\text{C}_8$ -cycloalkyl and  $\text{C}_1$ - to  $\text{C}_{20}$ -alkoxy radicals which may be interrupted and/or substituted by heteroatoms selected from N and O, it being possible for the heteroatoms in turn to carry substituents, preferably selected from H,  $\text{C}_1$ - $\text{C}_6$ -alkyl, aryl and hetaryl; or  $\text{R}^4$  and  $\text{R}^5$ , together with the N atom to which they are bonded, form a 5-, 6- or 7-membered cyclic structure which may have one or two heteroatoms selected from N and O and may be substituted by one, two or three  $\text{C}_1$ - to  $\text{C}_6$ -alkyl radicals. Furthermore,  $\text{R}^4$  and  $\text{R}^5$  may be aryl or hetaryl. Aryl and hetaryl radicals may have from one to three substituents selected, for example, from hydroxyl and the abovementioned alkyl, cycloalkyl or alkoxy radicals and polyisobutenyl radicals.

Examples of suitable radicals  $\text{R}^4$  and  $\text{R}^5$  are hydrogen, methyl, ethyl, n-propyl, sec-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, n-pentyl and n-hexyl, 5-, 6- and 7-membered saturated, unsaturated or aromatic carbocyclic and heterocyclic structures, such as cyclopentyl, cyclohexyl, phenyl, tolyl, xylyl, cycloheptyl, naphthyl, tetrahydrofuranyl, tetrahydropyranyl, dioxanyl, pyrrolidyl, piperidyl, pyridyl and pyrimidyl.

Suitable compounds of the formula  $\text{HNR}^4\text{R}^5$  which have exclusively a primary amino function are, for example, methylamine, ethylamine, n-propylamine, isopropylamine, n-butylamine, isobutylamine, sec-butylamine, tert-butylamine, pentylamine, hexylamine, cyclopentylamine, cyclohexylamine, aniline and benzylamine.

Suitable compounds of the formula  $\text{HNR}^4\text{R}^5$  which have exclusively a primary amino function and in which  $\text{R}^4$  or  $\text{R}^5$  is alkyl interrupted and/or substituted by the heteroatom O are, for example,  $\text{CH}_3\text{-O-C}_2\text{H}_4\text{-NH}_2$ ,  $\text{C}_2\text{H}_5\text{-O-C}_2\text{H}_4\text{-NH}_2$ ,  $\text{CH}_3\text{-O-C}_3\text{H}_6\text{-NH}_2$ ,  $\text{C}_2\text{H}_5\text{-O-C}_3\text{H}_6\text{-NH}_2$ ,  $\text{n-C}_4\text{H}_9\text{-O-C}_4\text{H}_8\text{-NH}_2$ ,  $\text{HO-C}_2\text{H}_4\text{-NH}_2$ ,  $\text{HO-C}_3\text{H}_7\text{-NH}_2$  and  $\text{HO-C}_4\text{H}_8\text{-NH}_2$ .

Suitable compounds of the formula  $\text{HNR}^4\text{R}^5$  which have exclusively a secondary amino function are, for example, dimethylamine, diethylamine, methylethylamine, di-n-propylamine, diisopropylamine, diisobutylamine, di-sec-butylamine, di-tert-butylamine, dipentylamine, dihexylamine, dicyclopentylamine, dicyclohexylamine and diphenylamine.

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Suitable compounds of the formula  $\text{HNR}^4\text{R}^5$  which have exclusively a secondary amino function and in which  $\text{R}^4$  and  $\text{R}^5$  are alkyl interrupted and/or substituted by the heteroatom O are, for example,  $(\text{CH}_3-\text{O}-\text{C}_2\text{H}_4)_2\text{NH}$ ,  $(\text{C}_2\text{H}_5-\text{O}-\text{C}_2\text{H}_4)_2\text{NH}$ ,  $(\text{CH}_3-\text{O}-\text{C}_3\text{H}_6)_2\text{NH}$ ,  $(\text{C}_2\text{H}_5-\text{O}-\text{C}_3\text{H}_6)_2\text{NH}$ ,  $(n-\text{C}_4\text{H}_9-\text{O}-\text{C}_4\text{H}_8)_2\text{NH}$ ,  $(\text{HO}-\text{C}_2\text{H}_4)_2\text{NH}$ ,  $(\text{HO}-\text{C}_3\text{H}_6)_2\text{NH}$  and  $(\text{HO}-\text{C}_4\text{H}_8)_2\text{NH}$ .

Suitable compounds of the formula HNR<sup>4</sup>R<sup>5</sup> in which R<sup>4</sup> and R<sup>5</sup>, together with the N atom to which they are bonded, form a 5-, 6- or 7-membered cyclic structure which may have one or two heteroatoms selected from N and O and may be interrupted by one, two or three C<sub>1</sub>- to C<sub>6</sub>-alkyl radicals are, for example, pyrrolidine, piperidine, morpholine and piperazine and their substituted derivatives, such as N-C<sub>1</sub>- to C<sub>6</sub>-alkylpiperazines and dimethylmorpholine.

Suitable compounds of the formula  $\text{HNR}^4\text{R}^5$  which have alkyl radicals interrupted and/or substituted by N are alkylatediamines, dialkylenetriamines, trialkylenetetramines and

20 polyalkylenepolyamines, such as oligo- or polyalkyleneimines, in particular oligo- and polyethyleneimines, preferably oligoethyleneimines, consisting of from 2 to 20, preferably from 2 to 10, particularly preferably 2 or 3, ethyleneimine units. In particular, those compounds, such as n-propylenediamine,

25 1,4-butanediamine, 1,6-hexanediamine, diethylenetriamine and triethylenetetramine, and their alkylation products, which have at least one primary or secondary amino function, e.g. 3-(dimethylamino)-n-propylamine, N,N-dimethylethylenediamine, N,N-diethylethylenediamine and

30 N,N,N',N'-tetramethyldiethylenetriamine, are suitable. Ethylenediamine is likewise suitable.

Further suitable compounds of the formula  $\text{HNR}^4\text{R}^5$  are the reaction products of alkylene oxides, in particular ethylene oxide, with primary amines, and copolymers of ethylene oxide with ethyleneimine and/or primary or secondary  $\text{C}_1$ - to  $\text{C}_6$ -alkylamines.

Preferred compounds of the formula  $\text{HNR}^4\text{R}^5$  are  
3-(dimethylamino)-n-propylamine,  
**40** di[3-(dimethylamino)-n-propyl]amine,  
di[3-(diethylamino)-n-propyl]amine,  
di[2-(dimethylamino)ethyl]amine, dimethylamine, diethylamine,  
di-n-propylamine, diisopropylamine, dicyclohexylamine,  
pyrrolidine, piperidine, morpholine, dimethylmorpholine,  
**45** N-methylpiperazine,  $\text{HO-C}_2\text{H}_4-\text{NH}_2$ ,  $(\text{HO-C}_2\text{H}_4)_2\text{NH}$ ,  $\text{H}_3\text{C-O-(CH}_2)_2-\text{NH}_2$ ,  
 $\text{H}_3\text{C-O-(CH}_2)_3-\text{NH}_2$ ,  $\text{HO-(CH}_2)_3-\text{NH}_2$ , diethylenetriamine,

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triethylenetetramine, N,N-diethylethylenediamine and N,N,N',N'-tetramethyldiethylenetriamine.

- Particularly preferred compounds of the formula HNR<sup>4</sup>R<sup>5</sup> are
- 5 3-(dimethylamino)-n-propylamine,  
di[3-(dimethylamino)-n-propyl]amine, dimethylamine, diethylamine, di-n-propylamine and morpholine.

The reaction temperatures suitable for the reaction b) depend on

10 a number of factors. In the case of the (Mannich) reaction in step b), water of reaction is formed. As a rule, this is removed from the reaction mixture. The water of reaction can be removed during the reaction, at the end of the reaction time or after the reaction is complete, for example by distillation.

15 Advantageously, the water of reaction can be removed by heating the reaction mixture in the presence of entraining agents. Examples of suitable entraining agents are organic solvents which form an azeotropic mixture with water and/or have a boiling point above the boiling point of water.

20 Particularly suitable entraining agents are paraffins, benzene and alkylaromatics, in particular toluene, xylenes and mixtures of alkylaromatics with other (high-boiling) hydrocarbons. As a rule, the water of reaction is removed at a temperature which

25 roughly corresponds to the boiling point of the entraining agent or of the azeotropic mixture of water and entraining agent.

Suitable temperatures for removing the water of reaction are therefore from 75 to 200°C, preferably from 80 to 180°C,

30 particularly preferably from 80 to 150°C, at atmospheric pressure. If the water of reaction is removed at reduced pressure, the temperature should be reduced in accordance with the lower boiling points.

35 The reaction temperatures for the (Mannich) reaction in step b) are preferably from 10 to 200°C, in particular from 20 to 180°C, e.g. about 35°C, about 90°C, about 120°C or about 140°C.

The reaction described under b) can be carried out, for example,

40 by combining polyisobutetylphenol, amine and formaldehyde source and bringing the reaction mixture to the desired reaction temperature, preferably into the abovementioned temperature ranges. The reaction described under b) can also be carried out by first adding the formaldehyde source to the

45 polyisobutetylphenol and, if required, a solvent and if necessary heating the mixture to the reaction temperature and then adding at least one secondary amine. The amine may be added in one

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portion or over a period of from 5 to 300, preferably from 10 to 150, minutes by adding a plurality of portions or continuous addition. The reaction described under b) can also be carried out by first combining polyisobut enylphenol and, if required, solvent 5 and amine, if necessary heating to the reaction temperature and then adding the formaldehyde source, it being possible to carry out the addition of the formaldehyde source as described above for the amine.

- 10 In a preferred embodiment, step b), i.e. the (Mannich) reaction and the removal of the water of reaction, is carried out at about atmospheric pressure and about 80°C, about 110°C or about 130°C using aromatic solvents, preferably toluene, xylenes or mixtures thereof, as entraining agents. Step b) is preferably carried out 15 by combining the reactants at from 10 to 50°C, if necessary mixing them for from 10 to 300 minutes in this temperature range and then bringing them, in the course of from 5 to 180, preferably from 10 to 120, minutes to the temperature required for removing the water of reaction by distillation.

20 The total reaction time for the conversion of the polyisobut enylphenols into the Mannich adducts in step b) is in general from 10 minutes to 24 hours, preferably from 30 minutes to 16 hours, particularly preferably from 60 minutes to 8 hours.

25 In the Mannich reaction carried out under b) or c), as a rule from 0.5 to 3.0, preferably from 0.5 to 2.0, in particular from 0.8 to 1.5, mol of formaldehyde (or a corresponding amount of a formaldehyde source) and from 0.5 to 3.0, preferably from 0.5 to 30 2.0, in particular from 0.8 to 1.5, mol of secondary amine, based on 1 mol of polyisobut enylphenol from a), are used.

The reactants formaldehyde source, secondary amine and polyisobut enylphenol in step b) are particularly preferably used 35 in a roughly equimolar ratio or a ratio of about 2:2:1 or about 1:2:1. As a rule, a substantially uniform product spectrum with a high proportion of amine-containing compounds can thus be achieved. A roughly equimolar ratio of the reactants and a 1:2:1 ratio of the reactants lead to the preferred formation of 40 monoaminomethylated compounds. A reactant ratio of about 2:2:1 leads to the preferred formation of bisaminomethylated compounds.

When the process is carried out as described under c), first an adduct of formaldehyde or a formaldehyde equivalent, such as 45 dichloromethane or dibromomethane or dimethoxymethane, an amine, and, if required, a solvent is prepared by combining the components and, if required, with heating to temperature ranges

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described above for b) and within the reaction times described above for b), preferably from 5 to 180, in particular from 10 to 90, minutes. During or after the reaction of amine and formaldehyde source, resulting water of reaction can if desired 5 be removed, for example as described above. The water can also be removed by water-binding agents, such as KOH, NaOH, CaO or Na<sub>2</sub>SO<sub>4</sub>. The reaction product thus obtained and comprising the amine and formaldehyde can, if desired, be purified and/or isolated. In particular, the adducts obtainable by reacting one equivalent of 10 formaldehyde or one equivalent of a formaldehyde equivalent with one or two equivalents of a secondary amine or one equivalent of a primary amine and after removal of the resulting water of reaction, alcohol or halide (secondary amine: methyleneiminium ion or aminal; primary amine: imine) can, if desired, be 15 isolated, purified and/or stored for a subsequent reaction with the polyisobut enylphenol. The reaction product obtained from amine and formaldehyde or formaldehyde equivalent and the polyisobut enylphenol are then mixed with one another, it being possible to carry out the combination in one portion, in a 20 plurality of portions or continuously in the periods stated above. Reaction temperatures and reaction times are usually in the ranges as described above for the reaction procedures according to b). If the reaction product obtained from formaldehyde or formaldehyde equivalent and amine is isolated, 25 the reaction with the polyisobut enylphenol is preferably carried out in such a way that the polyisobut enylphenol and, if required, the solvent are initially taken, the initially taken mixture is, if required, heated to a temperature of from 50 to 100°C and the adduct obtained from amine and formaldehyde or formaldehyde 30 equivalent is then added. Said adduct is then preferably added over a period of from 5 minutes to 10 hours, in particular from 10 minutes to 4 hours, and the reaction mixture is stirred for a further 10 minutes to 5 hours, preferably 30 minutes to 4 hours, to a suitable reaction temperature. If desired, the amine formed 35 in the reaction of aminals with the polyisobut enylphenol can be distilled off and/or removed under reduced pressure, depending on the volatility of the amine.

If the reaction described under c) is carried out without 40 isolating the adduct of formaldehyde or formaldehyde equivalent and amine(s), preferably the formaldehyde source or the formaldehyde equivalent and amine are first combined, if necessary heated and thoroughly mixed over a period of, as a rule, at least 5 minutes, preferably from 10 minutes to 4 hours, 45 in particular from 20 minutes to 60 minutes, and the polyisobut enylphenol is added to the adduct. For this purpose, the polyisobut enylphenol is preferably added to the adduct in the

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initially taken mixture. The mixture is preferably heated to a suitable reaction temperature for from 10 minutes to 6 hours, in particular from 30 minutes to 4 hours. Suitable reaction temperatures for this purpose are, for example, from 25 to 120°C,  
5 in particular from 50 to 100°C.

When using primary amines according to c), the adduct used is preferably an N-alkylmethylenimine which may have been isolated beforehand, the N-alkyl radical preferably being derived from the 10 abovementioned radicals R<sup>4</sup> or R<sup>5</sup>. Such N-alkylmethylenimines tend to trimerize, so that they usually include N,N',N''-trialkyltetrahydrotriazines. These mixtures, as well as pure tetrahydrotriazines, can also be used.

15 When secondary amines are used according to c), the adduct used is preferably a hemiaminal, methyleneiminium ion or aminal which may have been isolated beforehand, the amino functions of the hemiaminal, methyleneiminium ion or aminal preferably being derived from the abovementioned secondary amines  $\text{HNR}^4\text{R}'^5$ .

**20** The adduct used according to c) is preferably an adduct of at least one amine and a formaldehyde source, which adduct is obtained by reacting the two reactants for at least 15, for example about 30, about 60 or about 90, minutes at above +15°C,  
**25** preferably above +20°C, e.g. at from 20 to 30°C or from about 20 to 50°C. If required, subsequently formed water of reaction can be removed under the conditions as described above for b), for example by distillation or adsorption.

30 Suitable solvents for the reaction according to c) are the  
solvents and entraining agents described for the reaction  
according to b), and hydrocarbons and hydrocarbon mixtures having  
boiling points or boiling ranges of from +35 to +110°C, alcohols,  
 $C_2$ - $C_6$ -dialkyl ethers, cyclic mono- and diethers of 3 to 6 carbon  
35 atoms, in particular ethanol, isopropanol, butanols,  
tetrahydrofuran, tetrahydropyran and dioxane.

By means of the procedure described under c), it is possible in many cases to achieve a particularly uniform product spectrum substantially independently of the amine used, in particular if the reactants are used in about equimolar amounts or in a stoichiometric ratio of formaldehyde or formaldehyde equivalent, amine and polyisobut enylphenol of about 1:2:1 or about 2:2:1 or about 2:1:1.

## 15

The adduct used according to c) is preferably an aminal of formaldehyde with a secondary amine, selected from di-C<sub>1</sub>-C<sub>8</sub>-alkylamine whose alkyl groups may be substituted by an N(C<sub>1</sub>-C<sub>4</sub>-alkyl)<sub>2</sub> group, and cyclic amines which have 4 to 6 carbon atoms and whose cyclic structure may be interrupted by O and/or N-C<sub>1</sub>-C<sub>4</sub>-alkyl.

Suitable aminals for the reaction described above are, for example, N,N,N',N'-tetramethylmethylenediamine,  
10 N,N,N',N'-tetraethylmethylenediamine, bis{di[3-(dimethylamino)-n-propyl]amino}methane, bis(morpholino)methane and bis(4-methylpiperazino)methane.

In a further embodiment of step c), the polyisobut enylphenols can  
15 be subjected to an analogous reaction with hemiaminals to give Mannich adducts. Such hemiaminals are obtainable from formaldehyde sources or formaldehyde equivalents and secondary amines which have no primary amino function, and can be produced in a one-pot reaction in the presence of the  
20 polyisobut enylphenols (variant b)) or prepared separately (variant c)). Such hemiaminals can be etherified with C<sub>1</sub>-C<sub>12</sub>-alkanols or esterified with C<sub>1</sub>-C<sub>12</sub>-carboxylic acids. Suitable hemiaminals are, for example, N-hydroxymethylmorpholine and N-hydroxymethyldiisopropylamine.

25 By means of the procedures described above under b) and c), the polyisobut enylphenol can be converted into bisaminomethylated Mannich adducts through the choice of the stoichiometry. For the preparation of the bisadducts, formaldehyde (or a formaldehyde  
30 source or formaldehyde equivalent) and/or amines or imines, aminals or hemiaminals are preferably used in a two-fold to three-fold excess and, if required, the reaction time is prolonged.

35 In a preferred embodiment of the novel process, the formaldehyde source or the formaldehyde equivalent, preferably formalin solution or paraformaldehyde, is, if required, first initially taken in a solvent, and a roughly equimolar amount of a primary amine, preferably of an amine having only one primary and no  
40 secondary amino group, is added at from +15 to +50°C, preferably from +20 to +35°C. The mixture is then thoroughly mixed for from 5 to 90, preferably from 15 to 60, minutes at a temperature in the range stated above and is then combined with the polyisobut enylphenol from step a) and, if required, further  
45 solvent. Thereafter, the mixture thus obtained is heated, for example under reflux, for from 30 minutes to 6 hours, preferably from 1 to 3 hours, to a temperature of from 40 to 100°C,

preferably from 50 to 90°C. The reaction mixture can, if desired, then be purified, for example by filtration and/or removal of volatile components, for example under reduced pressure or by distillation.

5

In a further preferred embodiment of the novel process, the reaction product obtained under a) and, if required, solvent are initially taken and the mixture is heated to a temperature of from 40 to 100°C, preferably from 50 to 90°C, for example while 10 refluxing the solvent. Thereafter, either a roughly equimolar amount or from 1.7 to 2.5 equivalents, e.g. about 2 equivalents, of an aminal, for example a tetra-C<sub>1</sub>-C<sub>4</sub>-alkylmethylenediamine, if required in a solvent, is slowly added at this temperature, for example over a period of from 30 minutes to 6 hours, preferably 15 from 2 to 5 hours, and the reaction mixture is allowed to react for a further 30 minutes to 4 hours, in particular from 1 to 3 hours, at a temperature in the abovementioned ranges. If required, the reaction mixture can then be purified, for example by filtration and/or removal of the volatile components under 20 reduced pressure or by distillation.

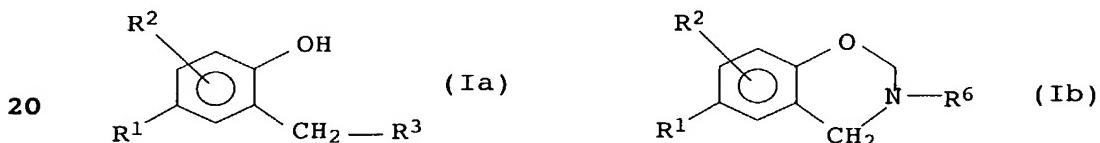
Suitable solvents for the two embodiments of step c) which are described above are hydrocarbons, hydrocarbon mixtures, ethers or alcohols having a boiling point or boiling range of from 40 to 25 100°C, in particular from 50 to 90°C. In particular, tetrahydrofuran und dioxane are suitable.

In a further preferred embodiment of the reaction of the reaction product obtained, polyisobut enylphenol from step a) and, if 30 required, solvent are first initially taken. Thereafter, about equimolar amounts of a formaldehyde source and of a secondary amine, preferably an amine having exclusively a secondary amino function, and, if required, solvent are slowly added, for example by dropwise addition. The components are then mixed for a further 35 20 minutes to 3 hours, preferably from 30 to 90 minutes, and the mixture is then heated for a further 30 minutes to 4 hours, preferably from 1 to 3 hours, to a temperature of from 40 to 100°C, preferably from 50 to 90°C. The reaction mixture can then be purified, for example with filtration and/or removal of the 40 volatile components under reduced pressure or by distillation. Suitable solvents are in particular the solvents stated in the preferred embodiments described above. Isopropanol is preferred.

In a further preferred embodiment, polyisobut enylphenol and a 45 roughly equimolar amount of a secondary amine, preferably having exclusively a secondary amino group, in a solvent are initially taken. Thereafter a roughly equimolar amount of a formaldehyde

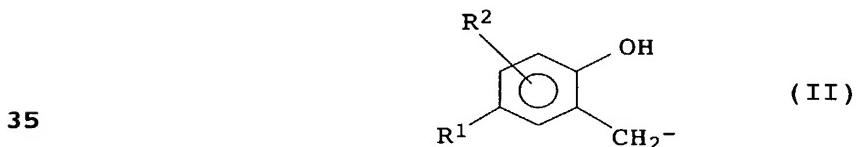
source is slowly added. The reaction mixture is preferably heated to a temperature of from 30 to 70°C, preferably from 40 to 60°C during the addition of the formaldehyde source. The reaction mixture is then heated for from 1 to 6, preferably from 2 to 4, 5 hours to a temperature of from 80 to 130°C, preferably from 90 to 120°C, particularly preferably until the solvent refluxes. The resulting water of reaction is preferably removed by distillation. Particularly suitable solvents for this embodiment are aromatic solvents or mixtures thereof with further 10 high-boiling hydrocarbons. Xylenes and toluene and mixtures thereof are particularly suitable, toluene being preferred.

As a rule, the novel processes give adduct mixtures which comprise at least 40, frequently at least 50, particularly 15 preferably at least 60, mol% of compounds of the formula Ia and/or Ib



where

R<sup>1</sup> is a terminally bonded polyisobut enyl radical,  
R<sup>2</sup> is H, C<sub>1</sub>- to C<sub>20</sub>-alkyl, C<sub>1</sub>- to C<sub>20</sub>-alkoxy, hydroxyl,  
25 a polyalkylene radical or CH<sub>2</sub>NR<sup>4</sup>R<sup>5</sup>, where R<sup>4</sup> and R<sup>5</sup> have the meanings stated below, and  
R<sup>3</sup> is NR<sup>4</sup>R<sup>5</sup>, where R<sup>4</sup> and R<sup>5</sup>, independently of one another, are selected from H, C<sub>1</sub>- to C<sub>20</sub>-alkyl, C<sub>3</sub>- to C<sub>8</sub>-cycloalkyl and C<sub>1</sub>- to C<sub>20</sub>-alkoxy radicals which may be interrupted and/or 30 substituted by heteroatoms selected from N and O, and phenol radicals of the formula II,



where R<sup>1</sup> and R<sup>2</sup> are as defined above; with the proviso that R<sup>4</sup> and R<sup>5</sup> are not simultaneously H or phenol radicals of the formula II; or R<sup>4</sup> and R<sup>5</sup>, together with the N atom to which they are bonded, form a 5-, 40 6- or 7-membered cyclic structure which has one or two heteroatoms selected from N and O and may be substituted by one, two or three C<sub>1</sub>- to C<sub>6</sub>-alkyl radicals; and R<sup>6</sup> is a radical R<sup>4</sup> or R<sup>5</sup> other than H.

## 18

The compounds of the formula Ib (dihydrobenzoxazines) can be formed in the presence of formaldehyde sources or formaldehyde equivalents from compounds of the formula Ia, where R<sup>4</sup> or R<sup>5</sup> is H.

- 5 Preferred radicals R<sup>1</sup> to R<sup>6</sup> are derived from the polyisobutenes, phenols, formaldehyde sources or formaldehyde equivalents and amines described above.

Preferably, the Mannich adducts of the formula Ia and/or Ib are  
 10 monomolecular polyisobutarylphenol-amines which have only one polyisobutarylphenol unit per molecule. Oligomeric polyisobutarylphenolamines having two, three or more polyisobutarylphenol units per molecule are formed only in a small amount, if at all.

15 In many cases, the novel process gives an adduct mixture which contains at least 40, frequently at least 50, particularly preferably at least 60, mol% of a compound selected from compounds of the formula Ia or Ib. The preferred embodiments of  
 20 the novel process can be a mixture of Mannich adducts or chemically uniform Mannich adducts which comprises at least 70 or at least 80 mol% of compounds of the formula Ia and/or Ib.

If desired, the products obtained by the novel processes may be  
 25 further purified, for example by extraction, distillation or column chromatography, in particular as described below.

The present invention furthermore relates to the Mannich adducts of the formulae Ia and Ib which are obtained by the novel  
 30 process, in the form of their pure substances.

In a preferred embodiment the adduct mixture comprises at least 40, in particular at least 50, particularly preferably at least 60, mol% of at least one compound selected from the N- or  
 35 N,N-substituted derivatives of N,N-bis(2-hydroxy-5-polyisobutarylbenzyl)amine (e.g. compounds of the formula Ia, where R<sup>2</sup> is H, R<sup>3</sup> is NR<sup>4</sup>R<sup>5</sup>, R<sup>4</sup> is a phenol radical of the formula II whose radical R<sup>2</sup> is likewise H, and R<sup>5</sup> is a radical other than H and other than phenol radicals of the  
 40 formula II), 2-aminomethyl-4-polyisobutarylphenols (e.g. compounds of the formula Ia, where R<sup>2</sup> is H, R<sup>3</sup> is NR<sup>4</sup>R<sup>5</sup>, R<sup>4</sup> and R<sup>5</sup> are radicals other than phenol radicals of the formula II and R<sup>4</sup> and R<sup>5</sup> are not simultaneously H),  
 45 2,6-bisaminomethyl-4-polyisobutarylphenols (e.g. compounds of the formula Ia, where R<sup>2</sup> is CH<sub>2</sub>NR<sup>4</sup>R<sup>5</sup> in the ortho position, R<sup>3</sup> is NR<sup>4</sup>R<sup>5</sup>, and R<sup>4</sup> and R<sup>5</sup> are radicals other than phenol radicals of the formula II and R<sup>4</sup> and R<sup>5</sup> are not simultaneously H) and

3,4-dihydro-1,3-2H-benzoxazines (e.g. compounds of the formula Ib, where R<sup>2</sup> is H and R<sup>6</sup> is a radical R<sup>4</sup> or R<sup>5</sup> other than H).

In a further preferred embodiment, the adduct mixture contains at least 40, in particular at least 50, particularly preferably at least 60, mol% of N- or N,N-substituted derivatives of 2-aminomethyl-4-polyisobut enylphenol (e.g. compounds of the formula Ia, where R<sup>2</sup> is H, R<sup>3</sup> is NR<sup>4</sup>R<sup>5</sup>, R<sup>4</sup> and R<sup>5</sup> are radicals other than phenol radicals of the formula II and R<sup>4</sup> and R<sup>5</sup> are not simultaneously H) and/or 3,4-dihydro-1,3-2H-benzoxazine (e.g. compounds of the formula Ib, where R<sup>2</sup> is H and R<sup>6</sup> is a radical R<sup>4</sup> or R<sup>5</sup> other than H). These are referred to as mono-Mannich adducts.

- 15 In a preferred embodiment, the Mannich adducts obtainable by the process of the invention include little if any alkylation product of step a) that has not been further reacted. Since the Mannich reaction is an equilibrium reaction, the product will normally include a residual fraction of alkylation products from step a).
- 20 The fraction in the Mannich adducts which is polyisobut enylphenol which has not been further reacted is typically from 0 to 20 mol%, usually from 1 to 15 mol%, especially from 5 to 10 mol%, based on the total amount of the adduct mixture obtained. The polyisobut enylphenol fraction can be set to a desired value via 25 the reaction management of steps b) and c) or customary separation processes. A preferred separation process is the hereinafter described column chromatography. Since, however, a residual fraction of alkylation products which have not been reacted further is surprisingly not troublesome and frequently 30 even advantageous, it is generally possible to dispense not only with inconvenient process measures for an ideally complete reaction in steps b) and c) but also with further separating steps.
- 35 The Mannich adduct mixtures described above, in particular the nitrogen-containing components can be fractionated by column chromatography over stationary phases. The fractionation can be effected by means of one-stage or multistage elution. Suitable eluents are, for example, hydrocarbons, alcohols, ketones, water 40 and mixtures thereof, to which bases, e.g. amines or alkalis, may be added. The fractionation can advantageously be carried out by multistage elution, preferably with at least one hydrocarbon and then at least one basic alcohol/water mixture.
- 45 Particularly suitable stationary phases are oxides, as are usual in column chromatography. Acidic oxides, such as acidic alumina, are preferred, acidic silica gel being particularly preferred. A

## 20

preferably used basic alcohol/water mixture is a mixture comprising

- a) from 75 to 99.5, in particular from 85 to 98, particularly preferably from 90 to 97, % by weight of at least one C<sub>2</sub>-C<sub>4</sub>-alcohol, in particular ethanol and/or isopropanol, particularly preferably isopropanol,
- b) from 0.4 to 24.4% by weight of water and
- c) from 0.1 to 15, in particular from 0.5 to 10, particularly preferably from 1 to 5, % by weight of at least one amine which is volatile at room temperature.

Suitable amines volatile at room temperature are, for example, ammonia, mono-C<sub>1</sub>-C<sub>8</sub>-alkylamines, di-C<sub>1</sub>-C<sub>6</sub>-alkylamines and tri-C<sub>1</sub>-C<sub>4</sub>-alkylamines, in particular ammonia, methylamine, ethylamine, n-propylamine, isopropylamine, dimethylamine, diethylamine, di-n-propylamine, diisopropylamine, di-n-butylamine, di-sec-butylamine, di-tert-butylamine, trimethylamine, triethylamine, diisopropylethylamine and triisopropylamine. Ammonia is particularly preferred.

As a rule, the fractionation is carried out by column chromatography in such a way that the adduct mixture is added to a column filled with a stationary phase and, if required, conditioned. If necessary, in a first step, the column with the added adduct mixture can then be washed with a nonpolar solvent, for example an aliphatic or aromatic hydrocarbon. This makes it possible, for example, to elute fractions not containing amines. The fractionation of the adduct mixture, in particular of the amine-containing components, is effected by, preferably, multistage elution with an alcohol/water mixture as described above. The elution can be carried out with an alcohol/water mixture of either constant composition or variable composition, for example by means of a one-stage or multistage gradient or a continuous gradient.

The process as described above can be used on the one hand for isolating those components of the adduct mixture which do not contain amines and then recovering the unfractionated amine-containing components of the adduct mixture. On the other hand, those components of the adduct mixture which do not contain nitrogen can, if required, be first isolated and the nitrogen-containing components then fractionated. With a suitable separation efficiency of the column used, the adduct mixtures can, if desired, be fractionated down to the individual compounds.

## 21

Preferably, adduct mixtures having a polydispersity of from 1.05 to 3.5, in particular from 1.1 to 2.5, particularly preferably from 1.1 to 1.9, are obtainable by the novel process.

- 5 The desired polydispersity can be established by a careful choice of the starting materials, choice of the stoichiometry, choice of the temperature and reaction time and possibly of the working up, in particular by conventional purification techniques, such as extraction and distillation and, if required, the novel  
10 fractionation by column chromatography.

Suitable measures which, individually or in combination, promote the formation of adduct mixtures having high activity and/or low polydispersity are, for example, selected from

- 15 - use of polyisobutenes of low polydispersity,  
- use of polyisobutenes having very high proportions of terminal double bonds,  
- use of the polyisobutenes in less than the stoichiometric  
20 amount in the alkylation of the phenols, if necessary followed by subsequent removal of the unconverted phenols,  
- carrying out the alkylation at a temperature which is as low as possible but still ensures complete conversion, for example at above about +5°C and below about +30°C,  
25 - maintaining a suitable stoichiometry, for example a formaldehyde source:amine:polyisobutylphenol ratio of about 1:1:1 or about 1:2:1 (for the preparation of mono-Mannich adducts) or 2:2:1 (for the preparation of bis-Mannich adducts) or 2:1:1 (leads to the formation of oxazines when  
30 primary amines are used) or 2:1:2, where in the last case a primary amine is preferably used (leads to the preparation of bisarylmonoamines),  
- carrying out the reaction of the reaction product obtained according to a) with an adduct of amine and formaldehyde or  
35 formaldehyde equivalent according to c), in particular according to the preferred embodiments described above,  
- removal of the adducts which do not contain amine from the mixture by fractionation by column chromatography,  
- fractionation of the amine-containing adducts of the mixture  
40 by column chromatography, preferably over acidic stationary phases by elution with basic alcohol/water mixtures.

The present invention furthermore relates to a Mannich adduct obtainable by a process as described above.

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The present invention also relates to a Mannich adduct containing at least one compound of the formula Ia and/or Ib.

The present invention also relates to the use of at least one above-defined Mannich adduct as a detergent additive in fuel and lubricant compositions, if necessary in combination with further conventional fuel and lubricant additives and in particular with the additional components described below.

- 10 Examples of such additional components are further additives having a detergent action or having an action which inhibits valve seat wear, these comprising at least one hydrophobic hydrocarbon radical having a number average molecular weight ( $M_N$ ) of from 85 to 20,000 and at least one polar group selected from

15 (a) mono- or polyamino groups having up to 6 nitrogen atoms, at least one nitrogen atom having basic properties,

20 (b) nitro groups, if required in combination with hydroxyl groups,

(c) hydroxyl groups in combination with mono- or polyamino groups, at least one nitrogen atom having basic properties,

25 (d) carboxyl groups or their alkali metal or alkaline earth metal salts,

(e) sulfo groups or their alkali metal or alkaline earth metal salts,

30 (f) polyoxy-C<sub>2</sub>- to C<sub>4</sub>-alkylene groups which are terminated by hydroxyl groups or mono- or polyamino groups, at least one nitrogen atom having basic properties, or by carbamate groups,

35 (g) carboxylic ester groups,

(h) groups derived from succinic anhydride and having hydroxyl and/or amino and/or amido and/or imido groups, and

40 (i) groups produced by conventional Mannich reaction of phenolic hydroxyl groups with aldehydes and mono- or polyamines.

Examples of the above additive components having a detergent action or having an action which inhibits valve seat wear are:

additives containing mono- or polyamino groups (a) are preferably polyalkenemono- or polyalkenepolyamines based on polypropene or on highly reactive (i.e. having predominantly terminal double bonds, generally in the  $\beta$ - and  $\gamma$ -positions) or conventional (i.e. 5 having predominantly central double bonds) polybutene or polyisobutene which have an  $M_N$  of from 300 to 5000 and were not obtained by the novel process. Such additives based on highly reactive polyisobutene, which can be prepared from the polyisobutene which may contain up to 20% by weight of n-butene 10 units by hydroformylation and reductive amination with ammonia, monoamines or polyamines, such as dimethylaminopropylamine ethylenediamine, diethylenetriamine, triethylenetetramine or tetraethylenepentamine, are disclosed in particular in EP-A 244 616. If polybutene or polyisobutene having predominantly 15 central double bonds (generally in the  $\beta$  and  $\gamma$  positions) is used as a starting material in the preparation of the additives, the preparation by chlorination and the subsequent amination or by oxidation of the double bond with air or ozone to give the carbonyl or carboxyl compound and subsequent amination under 20 reductive (hydrogenating) conditions is a possible method. Here, the amines used for the amination may be the same as those used above for the reductive amination of the hydroformylated highly reactive polyisobutene. Corresponding additives based on polypropene are described in particular in WO-A 94/24231.

25

Further preferred additives containing monoamino groups (a) are the hydrogenation products of the reaction products of polyisobutenes having an average degree of polymerization P of from 5 to 100 with oxides of nitrogen or mixtures of oxides of 30 nitrogen and oxygen, as described in particular in WO-A 97/03946.

Further preferred additives containing monoamino groups (a) are the compounds obtainable from polyisobutene epoxides by reaction with amines and subsequent dehydration and reduction of the amino 35 alcohols, as described in DE-A 196 20 262.

Additives containing nitro groups, if required in combination with hydroxyl groups (b), are preferably reaction products of polyisobutenes having an average degree of polymerization P of 40 from 5 to 100 or from 10 to 100 with oxides of nitrogen or mixtures of oxides of nitrogen and oxygen, as described in particular in WO-A 96/03367 and WO-A 96/03479. These reaction products are as a rule mixtures of pure nitropolyisobutanes (e.g.  $\alpha, \beta$ -dinitropolyisobutane) and mixed hydroxynitropolyisobutanes 45 (e.g.  $\alpha$ -nitro- $\beta$ -hydroxypolyisobutane).

## 24

Additives containing hydroxyl groups in combination with mono- or polyamino groups (c) are in particular reaction products of polyisobutene epoxides, obtainable from polyisobutene having preferably predominantly terminal double bonds and an  $M_N$  of from 5 300 to 5000, with ammonia or mono- or polyamines, as described in particular in EP-A 476 485.

- Additives containing carboxyl groups or their alkali metal or alkaline earth metal salts (d) are preferably copolymers of 10  $C_2$ - $C_{40}$ -olefins with maleic anhydride having a total molar mass of from 500 to 20,000, some or all of whose carboxyl groups have been converted into the alkali metal or alkaline earth metal salts and a remainder of the carboxyl groups have been reacted with alcohols or amines. Such additives are disclosed in 15 particular in EP-A 307 815. Such additives serve mainly for preventing valve seat wear and, as described in WO-A 87/01126 can advantageously be used in combination with conventional fuel detergents, such as poly(iso)buteneamines or polyetheramines.
- 20 Additives containing sulfo groups or their alkali metal or alkaline earth metal salts (e) are preferably alkali metal or alkaline earth metal salts of an alkyl sulfosuccinate, as described in particular in EP-A 639 632. Such additives serve mainly for preventing valve seat wear and can advantageously be 25 used in combination with conventional fuel detergents, such as poly(iso)buteneamines or polyetheramines.

- Additives containing polyoxy- $C_2$ - to  $C_4$ -alkylene groups (f) are preferably polyethers or polyetheramines, which are obtainable by 30 reaction of  $C_2$ - to  $C_{60}$ -alkanols,  $C_6$ - to  $C_{30}$ -alkanediols, mono- or di- $C_2$ - $C_{30}$ -alkylamines,  $C_1$ - $C_{30}$ -alkylcyclohexanols or  $C_1$ - $C_{30}$ -alkylphenols with from 1 to 30 mol of ethylene oxide and/or propylene oxide and/or butylene oxide per hydroxyl group or amino group and, in the case of the polyetheramines, by subsequent 35 reductive amination with ammonia, monoamines or polyamines. Such products are described in particular in EP-A 310 875, EP-A 356 725, EP-A 700 985 and US-A 4 877 416. In the case of polyethers, such products also have carrier oil properties. Typical examples of these are tridecanol butoxylates, 40 isotridecanol butoxylates, isononylphenol butoxylates and polyisobutenol butoxylates and propoxylates and the corresponding reaction products with ammonia.

- Additives containing carboxylic ester groups (g) are preferably 45 esters of mono-, di- or tricarboxylic acids with long-chain alkanols or polyols, in particular those having a minimum viscosity of 2 mPas at 100°C, as described in particular in DE-A

25

- 38 38 918. The mono-, di- or tricarboxylic acids used may be aliphatic or aromatic acids, and particularly suitable ester alcohols or ester polyols are long-chain members having, for example, 6 to 24 carbon atoms. Typical members of the esters are  
5 adipates, phthalates, isophthalates, terephthalates and trimellitates of iso-octanol, of isononanol, of isodecanol and of isotridecanol. Such products also have carrier oil properties.

Additives containing groups derived from succinic anhydride and  
10 having hydroxyl and/or amino and/or amido and/or imido groups (h) are preferably corresponding derivatives of polyisobutylene succinic anhydride, which are obtainable by reaction of conventional or highly reactive polyisobutene having an  $M_N$  of from 300 to 5000 with maleic anhydride by a thermal  
15 method or via the chlorinated polyisobutene. Of particular interest here are derivatives with aliphatic polyamines, such as ethylenediamine, diethylenetriamine, triethylenetetramine or tetraethylenepentamine. Such gasoline fuel additives are described in particular in US-A 4 849 572.

20 Additives containing groups produced by conventional Mannich reaction of phenolic hydroxyl groups with aldehydes and mono- or polyamines (i) are preferably reaction products of polyisobutene-substituted phenols with formaldehyde and primary  
25 mono- or polyamines, such as ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine or dimethylaminopropylamine. Such polyisobutene Mannich bases are described in particular in EP-A 831 141.

30 For a more exact definition of the individual gasoline fuel additives mentioned, the disclosures of the abovementioned prior art publications are hereby expressly incorporated by reference.

Suitable solvents or diluents (in the preparation of additive  
35 packets) are aliphatic and aromatic hydrocarbons, e.g. solvent naphtha.

Further conventional additive components which can be combined with the novel additives are, for example, corrosion inhibitors,  
40 for example based on ammonium salts of organic carboxylic acids, which salts tend to form films, on heterocyclic aromatics, antioxidants or stabilizers, for example based on amines, such as p-phenylenediamine, dicyclohexylamine or derivatives thereof or on phenols, such as 2,4-di-tert-butylphenol or  
45 3,5-di-tert-butyl-4-hydroxyphenylpropionic acid, demulsifiers, antistatic agents, metallocenes, such as ferrocene or methylcyclopentadienylmanganese tricarbonyl, lubricity additives,

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such as specific fatty acids, alkenylsuccinic esters, bis(hydroxyalkyl)-fatty-amines, hydroxyacetamides or castor oil, and markers. If required, amines are also added for reducing the pH of the fuel.

5

Carrier oils, too, may be mentioned as further conventional components. Examples of these are mineral carrier oils (base oils), in particular those of the viscosity class solvent neutral (SN) 500 to 2000, synthetic carrier oils based on olefin polymers having an  $M_N$  of from 400 to 1800, especially those based on polybutene or on polyisobutene (hydrogenated or unhydrogenated), on poly-alpha-olefins or poly(internal)olefins, and synthetic carrier oils based on alkoxylated long-chain alcohols or phenols. Polyalkenyl alcohol-polyetheramines, as described, for example, in DE-199 16 512.2, are also suitable as further additives.

The present invention furthermore relates to additive concentrates, in particular fuel additive concentrates and lubricant additive concentrates, particularly preferably fuel additive concentrates, containing, in addition to conventional additive components as defined above, at least one novel Mannich adduct in amounts of from 0.1 to 99.9, preferably from 0.5 to 80, in particular from 1.0 to 60, % by weight, based on the total weight of the concentrate.

25

The present invention furthermore relates to fuel compositions, especially gasoline fuel compositions, which contain the novel Mannich adducts, in particular Mannich adducts of the formula I, in effective amounts. In the case of fuel compositions, effective amounts are to be understood as a rule as meaning from 10 to 5000, in particular from 50 to 2000, ppm by weight, based on the total amount of the fuel composition.

The present invention also relates to lubricant compositions, in particular lubricant compositions which contain from 0.1 to 10, in particular from 0.5 to 5, % by weight, based on the total amount of the lubricant composition, of the novel Mannich adducts, in particular Mannich adducts of the formula Ia and/or Ib.

40

The novel polyisobutylphenol-containing Mannich adducts, in particular polyisobutylphenol-containing Mannich adducts of the formula I, have a high uniformity, a narrow molecular weight distribution and/or a high proportion of amine-containing compounds. As further illustrated in the following experimental section, they have an excellent action as gasoline fuel detergents which clean valves and keep valves clean. In addition,

they do not have the initially described disadvantages of the polyalkylenylphenol Mannich adduct mixtures known from the prior art. Moreover, they have very advantageous viscosity behavior, in particular at low temperatures, which prevents formulation and 5 application problems, e.g. sticking of valves.

#### Examples

The alkylation products and the Mannich adducts were 10 characterized by means of  $^1\text{H-NMR}$  spectroscopy. For some of the Mannich adducts, only the chemical shifts ( $\delta$  in ppm) of the characteristic signals of the methylene protons of the aminomethylene group are reported.

#### 15 I. Preparation of the polyisobutenylphenols

##### Ia. Alkylation with a polyisobutene having $M_N = 550$

404.3 g of phenol were melted in a nitrogen atmosphere at from 40 20 to 45°C in a 4 l four-necked flask. 191 g of  $\text{BF}_3$ -diethyl ether adduct were added dropwise and the mixture was cooled to 10°C. 1100 g of polyisobutene having an  $M_N$  of 550 and a dimethylvinylidene content of 85%, dissolved in 1000 ml of hexane, were added dropwise in the course of 150 minutes at from 25 5 to 10°C. The mixture was allowed to warm up to room temperature in the course of 4 hours and was stirred overnight. The reaction was stopped by adding 1200 ml of 25% strength ammonia solution. The organic phase was separated off and then washed 8 times with 500 ml of water and dried over  $\text{NaSO}_4$ , and the solvent and small 30 amounts of phenol were removed under reduced pressure: 1236 g of oil (polyisobutenylphenol).

$^1\text{H-NMR}$ : 7.2 ppm (doublet, 2H), 6.7 ppm (doublet, 2H), 4.8 ppm (singlet, 1H), 1.75 ppm (singlet, 2H), 1.5-0.5 ppm (singlets, 35 78H).

This corresponds to an  $M_N$  of 550 for the alkyl radical. The signal range of 7.1-6.75 ppm contains small signals which indicate the formation of from 5 to 10% of 2- or 2,4-substituted phenol.

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##### Ib. Alkylation with a polyisobutene having $M_N = 1000$

203.9 g of phenol were melted under nitrogen at from 40 to 45°C in a 4 l four-necked flask. 95.5 g of  $\text{BF}_3$ -diethylether adduct were 45 added dropwise and the mixture was cooled to 20 to 25°C. 998 g of polyisobutene having an  $M_N$  of 1000 and a dimethylvinylidene content of 85%, dissolved in 1800 ml of hexane, were added

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dropwise in the course of 3 hours at from 20 to 25°C. Stirring was carried out overnight. The reaction was then stopped by adding 500 ml of 25% strength ammonia solution. The organic phase was separated off and then washed 7 times with 500 ml of water and dried over NaSO<sub>4</sub>, and the solvent was removed under reduced pressure: 1060 g of oil (polyisobut enylphenol).

<sup>1</sup>H-NMR: 7.2 ppm (doublet, 2H), 6.7 ppm (doublet, 2H), 4.8 ppm (singlet, broad 1H), 1.75 ppm (singlet, 2H), 1.5-0.5 ppm (singlets, 165H).

This corresponds to an M<sub>N</sub> of 1150 for the alkyl radical. The range from 7.1 to 6.75 contains small signals which indicate that, in addition to the main product (para-polyisobut enylphenol), from 5 to 10% of 2,4-substituted phenol had formed, which is in agreement with the small increase in molecular weight found.

## Ic.

76.1 g of phenol were melted under nitrogen at from 40 to 45°C in a 4 l four-necked flask. 28.4 g of BF<sub>3</sub>-diethylether adduct were added dropwise and the mixture was cooled to 20 to 25°C. 914.5 g of polyisobutene having an M<sub>N</sub> of 2300 and a dimethylvinylidene content of 85%, dissolved in 1000 ml of hexane, were added dropwise in the course of 3 hours at from 20 to 30°C. Stirring was carried out overnight. The reaction was then stopped by adding 500 ml of 25% strength ammonia solution. The organic phase was separated off and then washed 7 times with 500 ml of water and dried over NaSO<sub>4</sub>, and the solvent was removed under reduced pressure: 912 g of oil (polyisobut enylphenol).

<sup>1</sup>H-NMR: 7.2 ppm (doublet, 2H), 6.7 ppm (doublet, 2H), 4.8 ppm (singlet, broad 1H), 1.75 ppm (singlet, 2H), 1.5-0.5 ppm (singlets, 330H).

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This corresponds to an M<sub>N</sub> of 2310 for the alkyl radical.

## II. Conversion of the polyisobut enylphenols into Mannich adducts

## IIa.

320 g of polyisobut enylphenol from Example Ia in 200 ml of toluene were initially taken in a 4 l four-necked flask with a water separator. 43.9 g of morpholine were added, and 40.9 g of 37% strength formalin solution were added dropwise at 50°C under nitrogen as an inert gas. Thereafter the reaction mixture was heated until the solvent refluxed, and water was removed in the

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course of 3 hours by distillation. The solution was filtered and the solvent was removed under reduced pressure: 352 g of oil (Mannich adduct).

5  $^1\text{H-NMR}$ : 7.1 ppm (doublet, fine resolution, 1H), 6.9 ppm (singlet, fine resolution, 1H), 6.7 ppm (doublet, 1H), 3.8 ppm (4 multiplet, 4H), 3.7 ppm (singlet, 2H), 2.5 ppm (singlet, broad, 4H), 1.75 ppm (singlet, 2H), 1.5-0.5 ppm (singlets, 135H).

## 10 IIb.

260 g of polyisobutenyphenol from Example Ia were initially taken in a 1 l four-necked flask with a water separator. 12.6 g of paraformaldehyde in 74.8 g of  
15 di[3-(dimethylamino)-n-propyl]amine in 100 ml of isopropanol were then added dropwise, the temperature of the reaction mixture increasing to 38°C. The reaction mixture was stirred for 1 hour and was then refluxed for 2 hours. The reaction solution was filtered and the solvent ws removed under reduced pressure: 332 g  
20 of oil (Mannich adduct).

1  $^1\text{H-NMR}$ : 7.1 ppm (doublet, fine resolution, 1H), 6.9 ppm (singlet, fine resolution, 1H), 6.6 ppm (doublet, 1H), 3.7 ppm (singlet, 1.5H), 3.7-3.2 ppm (3 singlets, 0.5H), 2.5 ppm (triplet, 4H),  
25 2.2 ppm (triplett, 4H), 2.1 ppm (singlet, 12H), 1.75 ppm (singlet, 2H), 1.7 ppm (multiplet, 4H), 1.5-0.5 ppm (singlets, 78H).

These integrals correspond to a molecular weight  $M_N$  of 546 for the  
30 alkyl radical.

## IIc.

7.5 ml of 37% strength formalin solution in 30 ml of  
35 tetrahydrofuran were initially taken in a 500 ml four-necked flask. 3-(Dimethylamino)-n-propylamine was then added at from 20 to 25 °C. Stirring was carried out for a further 30 minutes at this temperature, and 120 g of polyisobutenyphenol from Example Ia were then added. The reaction mixture was then refluxed for  
40 2 hours. The reaction solution obtained was filtered and the solvent was removed under reduced pressure: 116 g of oil (Mannich adduct).

1  $^1\text{H-NMR}$ : 7.1 ppm (doublet, fine resolution, 1H), 6.9 ppm (singlet, fine resolution, 1H), 6.6 ppm (doublet, 1H), 3.9 ppm (singlet, 2H), 2.5 ppm (triplet, 2H), 2.2 ppm (triplet, 2H), 2.1 ppm

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(singlet, 4.5H), 1.75 ppm (singlet, 2H), 1.7 ppm (multiplet, 2H), 1.5-0.5 ppm (singlets, 141H).

## IIId.

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105 g of polyisobut enylphenol from Example Ib in 50 ml of tetrahydrofuran were initially taken in a 500 ml four-necked flask. The mixture was refluxed (from 75 to 80°C), and 20.4 g of tetramethylmethylenediamine in 75 ml of tetrahydrofuran were 10 added dropwise in the course of 4 hours and refluxing was continued for a further 2 hours. The solution was filtered and the solvent was removed under reduced pressure: 105 g of oil (Mannich adduct).

15  $^1\text{H-NMR}$ : 7.1 ppm (doublet, fine resolution, 1H), 6.9 ppm (singlet, fine resolution, 1H), 6.7 ppm (doublet, 1H), 3.6 ppm (singlet, 2H), 2.25 ppm (singlet, 6H), 1.75 ppm (singlet, 2H), 2.2 ppm (triplet, 4H), 2.1 ppm (singlet, 12H), 1.75 ppm (singlet, 2H), 1.5-0.5 ppm (singlets, 141H)

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These spectroscopic data correspond to an  $M_N$  of 987 for the alkyl radical.

## IIe.

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119.4 g of polyisobut enylphenol from Example Ic and 100 ml of toluene were initially taken in a 0.5 l four-necked flask provided with a water separator. 4.8 g of morpholine were added, and 4.5 g of 37% strength formalin solution were added dropwise 30 under nitrogen as an inert gas. Thereafter, the mixture was heated to reflux and water was removed by distillation in the course of 3 hours with vigorous refluxing. Thereafter, the solution was filtered and the solvent was removed under reduced pressure: 106 g of oil (Mannich adduct).

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$^1\text{H-NMR}$ : 7.1 ppm (doublet, fine resolution, 1H), 6.9 ppm (singlet, fine resolution, 1H), 6.7 ppm (doublet, 1H), 3.8 ppm (multiplet, 4H), 3.7 (multiplet, 2H), 2.5 ppm (singlet, 4H), 1.75 ppm (singlet, 2H), 1.5-0.5 ppm (singlets, 325H)

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## IIIf.

350 g of polyisobut enylphenol from Example Ib and 16 g of dimethylamine (40 ml of 40% strength aqueous solution) in 200 ml 45 of toluene were initially taken in a 1 l four-necked flask with a water separator. 29 ml of 37% strength aqueous solution of formaldehyde were added dropwise at 20 - 30°C and refluxing was

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carried out. Water was then removed in the course of 3 hours. The solution was filtered and the solvent was removed under reduced pressure: 355 g of oil.

5  $^1\text{H-NMR}$ : 7.1 ppm (doublet, fine resolution, 1H), 6.9 ppm (singlet, fine resolution, 1H), 6.7 ppm (doublet, 1H), 3.65 ppm (singlet, 2H), 2.1 ppm (singlet, 6H), 1.75 ppm (singlet, 2H), 1.5-0.5 ppm (singlets, 138H)

## 10 IIg.

A 1 l four-necked flask was charged with 151.7 g of tert-butylamine. After cooling to 20.4°C in an ice bath, 177.7 g of 37% formaldehyde solution were added dropwise at a temperature 15 in the range from 20.5 to 24.9°C over 30 minutes. 50 g of KOH pastilles were then added, and the resulting oil layer was separated off. The oil was treated once more with 50 g of KOH pastilles, separated off and filtered to obtain 145 g of a light-colored oil (N-tert-butylmethylenimine which, according to 20  $^1\text{H-NMR}$ , included 20% of N,N',N''-tri-tert-butylhexahydro-1,3,5-triazine).

1  $^1\text{H-NMR}$  of tert-butylmethylenimine: 7.25 ppm (quartet, 2H), 1.2 ppm (singlet, 9H),  
25  $^1\text{H-NMR}$  of N,N',N''-tri-tert-butylhexahydro-1,3,5-triazine: 3.5 ppm (singlet, 6H), 1.15 ppm (singlet, 27H)

A 250 ml four-necked flask was charged with 108 g of PIB-phenol from Example Ib, and 9.5 g of tert-butylmethylenimine were added 30 dropwise at 25°C. Stirring at 40°C for 3 hours was followed by taking up with 100 ml of hexane and washing 3 times with methanol. The solvent was stripped off at 100°C and 20 mbar: 90 g of oil.

35  $^1\text{H-NMR}$ : 7.1 ppm (doublet, fine splitting, 1H), 6.9 ppm (singlet, fine splitting, 1H), 6.7 ppm (doublet, 1H), 3.95 ppm (singlet, 2H), 1.75 ppm (singlet, 2H), 1.2 ppm (singlet, 9H), 1.5-0.5 ppm (singlets, 138H).

## 40 IIh.

A 1 l four-necked flask was charged with 153 g of N,N-dimethylaminopropylamine. After cooling to 20.4°C in an ice bath, 130 g of 37% formaldehyde solution were added dropwise at a 45 temperature in the range from 20 to 25°C over 30 minutes. 50 g of KOH pastilles were then added, and the resulting oil layer was separated off. The oil was treated once more with 50 g of KOH

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pastilles, separated off and filtered to obtain 145 g of a light-colored oil (*N,N',N''-tris(N,N-dimethylaminopropyl)hexahydro-1,3,5-triazine*).

5 <sup>1</sup>H-NMR of *N,N',N''-tris(N,N-dimethylaminopropyl)hexahydro-1,3,5-triazine*: 3.3 ppm (singlet, 6H), 2.4 ppm (triplet, 6H), 2.25 ppm (triplet, 6H), 2.2 ppm (singlet, 18H), 1.6 ppm (multiplet, 6H).

10 A 250 ml four-necked flask was charged with 110 g of PIB-phenol from Example Ib, and 11.5 g of *N,N',N''-tris(dimethylamino-propyl)hexahydro-1,3,5-triazine* were added dropwise at 25°C. Stirring at 80°C for 3 hours was followed by taking up with 100 ml of hexane, washing 3 times with water and drying with Na<sub>2</sub>SO<sub>4</sub>. The 15 solvent was stripped off at 100°C and 20 mbar: 95 g of oil.

<sup>1</sup>H-NMR: 7.1 ppm (doublet, fine splitting, 1H), 6.9 ppm (singlet, fine splitting, 1H), 6.7 ppm (doublet, 1H), 3.9 ppm (singlet, 2H), 2.4 ppm (triplet, 2H), 2.25 ppm (triplet, 2H), 2.2 ppm

20 (singlet, 6H), 1.75 ppm (singlet, 2H), 1.2 ppm (singlet, 9H), 1.6 ppm (multiplet, 2H), 1.5-0.5 ppm (singlets, 138H).

The Mannich adducts of the following Table 1 were prepared similarly to the preparative method of Example IIa.

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Table 1

Example No.	M <sub>n</sub> Polyisobutylene radical	Amine	PIB-phenol 1)	Amine [mol]	Formaldehyde [mol]	Yield [g]	δ of amino- methylene protons [ppm]
1	2300	DMAPA 3)	0.05	0.055	0.055	115	3.9
2	2300	NMPIP 4)	0.05	0.11	0.11	109	3.7
3	2300	Morpholine	0.05	0.055	0.055	106	3.7
4 1)	550	DEOHA 5)	0.167	0.33	0.35	136	3.7
5	750	DMAPA	0.27	0.29	0.29	254	3.9
6	1300	DMA 6)	0.26	0.34	0.32	360	3.6
7	250	DETA 7)	0.43	1.03	0.95	260	3.9 + 3.75
8	550	DMA	0.39	0.5	0.47	266	3.6
9	700	DMA	0.44	0.57	0.53	369	3.6
10	1000	DEA 8)	0.1	0.12	0.12	112	3.72 + 3.64
11	1000	DPA 9)	0.1	0.12	0.12	113	3.77
12 2)	1000	DMA	0.1	0.13	0.13	116	3.55
13 2)	1000	DEA	0.084	0.11	0.11	89	3.68
14 2)	1000	DPA	0.073	0.1	0.1	84	3.7
15	1000	TMPDA 10)	0.1	0.15	0.13	119	3.67
16 1)	1000	DEOHA	0.1	0.12	0.11	115	3.8
17 1)	1000	DEOHA	0.1	0.24	0.3	118	3.75

Example No.	M <sub>n</sub> Polyisobutylene radical	Amine	PIB-phenol 11)	Amine [mol]	Formaldehyde [mol]	Yield [g]	δ of amino- methylene protons [ppm]
18	700	DEOHA	0.43	0.47	0.47	366	3.6
19 1)	224	DEOHA	0.25	0.8	0.9	166	3.7
20 1)	224	DEOHA	0.25	0.27	0.3	106	3.75
21 1)	2300	DEOHA	0.025	0.027	0.03	64	3.75
22 1)	2300	DEOHA	0.025	0.08	0.09	69	3.7

- 1) Paraformaldehyde was used instead of 37% formaldehyde solution
- 2) 2-Methyl-4-polyisobutylene was used instead of 37% formaldehyde solution
- 3) 3-(Dimethylamino)-n-propylamine
- 4) N-Methylpiperazine
- 5) Diethanolamine
- 6) Dimethylamine
- 7) Diethylenetriamine
- 8) Diethylamine
- 9) Dipropylamine
- 10) Trimethylpropylenediamine
- 11) Polyisobutylenephenol

### III. Testing of the performance characteristics

The lubricant used below was in each case reference oil RL 189/5.

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IIIa.

The intake valve cleanliness was tested by CEC method F-05-A-93 in an Opel Kadett engine. Commercial European premium grade base fuel according to EN 228, to which either no fuel additive (comparative example 1) or fuel additives not according to the invention and based on Mannich adducts (comparative example 2) or a novel polyisobutenyphenol-containing Mannich adduct (Example 1) had been added, was used for this purpose.

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The fuel additive not according to the invention and from comparative example 2 was prepared according to comparative example 2 of EP-A-0 831 141.

**20** The novel polyisobut enylphenol-containing Mannich adduct from Example B1 was prepared according to Ia and IIc.

The novel polyisobutlenylphenol-containing Mannich adduct of Example B2 was prepared according to Ib and IIIf.

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The most important parameters, the dosage and the performance results, are summarized in Table 2.

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Table 2

	M <sub>N</sub> <sup>1)</sup>	Amine	Dosage [mg/kg]	Valve deposits [mg/valve]				Mean value <sup>2)</sup>
				1	2	3	4	
Comp. 1	-	-	-	450	188	316	366	330
Comp. 2	1000	EDA <sup>3)</sup>	400	9	127	7	193	84
Inv. 1	550	DMAPA <sup>4)</sup>	400	0	1	0	0	0.25
Inv. 2	1000	DMA <sup>5)</sup>	300	0	0	0	0	0

- 1) Number average molecular weight of the polyisobutylene radical  
 2) Mean value of the deposits from the four valves  
 3) Ethylenediamine  
 4) 3-(Dimethylamino)-n-propylamine  
 5) Dimethylamine

## IIIB.

- The intake valve cleanliness was tested by CEC method F-04-A-87  
 5 in an Opel Kadett engine using a commercial European premium grade base fuel according to EN 228 either without fuel additive (Comparative Example 3), or with a noninventive fuel additive based on a polyisobut enylamine obtainable by hydroformylation and subsequent reductive amination of a polyisobutene (Comparative  
 10 Example 4) or with inventive polyisobut enylphenol-containing Mannich adducts (Inventive Examples 3 and 4). The additive was used in the form of a 50% by weight solution in a C<sub>10</sub>-C<sub>13</sub>-paraffin.  
 15 Some parameters of the additives used, the dosage and the performance results are summarized in Table 3.

Table 3

	Example No.	M <sub>n</sub> 1)	Amine	Dosage [mg/kg]	Δ IVD 2) [mg/valve]
20	Comp. 3	-	-	300	442
	Comp. 4	1000	NH <sub>3</sub>	300	75
25	Inv. 3	1000	DMAPA 3)	300	3
	Inv. 4	1000	DMA 4)	300	2

- 1) Number average molecular weight of polyisobut enyl radical  
 2) IVD = intake valve deposits; mean of deposits on all valves  
 3) 3-(Dimethylamino)-n-propylamine  
 30 4) Dimethylamine

## IIIC.

- The intake valve cleanliness was tested by CEC method F-05-A-93  
 35 in a Mercedes Benz M 102 E engine using a commercial European premium grade base fuel according to EN 228 either without fuel additive (Comparative Example 5) or with a fuel additive mixture comprising 41% by weight of a synthetic carrier oil (based on a polybutoxylated fatty alcohol) and 59% by weight of a  
 40 noninventive (Comparative Example 6) or an inventive polyisobut enylphenol-containing Mannich adduct (Inventive Example 5). The Mannich adducts were used in the form of a 50% by weight solution in a C<sub>10</sub>-C<sub>13</sub>-paraffin.

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The noninventive fuel additive used was a polyisobut enylphenol-containing Mannich adduct based on a conventional polyisobutene, phenol and dimethylaminopropylamine.

5 The essential parameters, the dosage and the performance results are summarized in Table 4.

Table 4

10	Example No.	M <sub>n</sub> 1)	Amine	Dosage [mg/kg]	Δ IVD 2) [mg/valve]
15	Comp. 5	-	-	600	298
20	Comp. 6	1000	DMAPA 3)	600	194
25	Inv. 5	1000	DMAPA	600	53

- 1) Number average molecular weight of polyisobut enyl radical  
 2) IVD = intake valve deposits; mean of deposits on all valves  
 3) 3-(Dimethylamino)-n-propylamine

30 IIIId.

The intake valve cleanliness was tested by CEC method F-05-A-93 in a Mercedes Benz M 102 E engine using a commercial European premium grade base fuel according to EN 228 either without fuel additive (Comparative Example 7) or with a fuel additive mixture comprising 40% by weight of a synthetic carrier oil (based on a polybutoxylated fatty alcohol) and 60% by weight of a noninventive (Comparative Example 8) or an inventive polyisobut enylphenol-containing Mannich adduct (Inventive Examples 6 to 12). The Mannich adducts were used in the form of a 50% by weight solution in a C<sub>10</sub>-C<sub>13</sub>-paraffin.

35 The noninventive fuel additive used was a polyisobut enylamine obtainable by hydroformylation and subsequent reductive amination of a polyisobutene.

The essential parameters, the dosage and the performance results are summarized in Table 5.

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Table 5

Example No.	$M_n$ <sup>1)</sup>	Reactant content [wt%]	Bis(amino-methyl) derivate content [wt%]	Amine	Dosage [mg/kg]	$\Delta$ IVD <sup>2)</sup>
						[mg/valve]
Comp. 7	-	-	-	-	400	277
Comp. 8	1000	-	-	NH <sub>3</sub>	400	27
Inv. 6	1000	4	2	DMA <sup>3)</sup>	400	8
Inv. 7	1000	1	3	DMA	400	13
Inv. 8	1000	9	0	DMA	400	1
Inv. 9	1000	0	24	DMA	400	16
Inv. 10	1000	-	-	DPA <sup>4)</sup>	400	9
Inv. 11	1000	-	-	DEA <sup>5)</sup>	400	10
Inv. 12 <sup>6)</sup>	1000	-	-	DMA	400	14

1) Number average molecular weight of polyisobutetyl radical

20 2) IVD = intake valve deposits; mean of deposits on all valves

### 3) Dimethylamine

4) Dipropylamine

### 5) Diethylamine

6) Cresol was used instead of phenol in the aminoalkylation

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The intake valve cleanliness was tested by CEC method F-05-A-93 in a Mercedes Benz M 102 E engine using a commercial European premium grade base fuel according to EN 228 either without fuel additive (Comparative Example 9) or with a fuel additive mixture comprising 40% by weight of a synthetic carrier oil (based on a propoxylated fatty alcohol) and 60% by weight of a noninventive fuel additive (Comparative Example 10) or an inventive polyisobutenylphenol-containing Mannich adduct (Inventive Example 13). The fuel additives were used in the form of a 50% by weight solution in a C<sub>10</sub>-C<sub>13</sub>-paraffin.

The noninventive fuel additive used was a polyisobut enylamine obtainable by hydroformylation and subsequent reductive amination of a polyisobutene.

The essential parameters, the dosage and the performance results are summarized in Table 6.

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Table 6

Example No.	M <sub>n</sub> 1)	Amine	Dosage [mg/kg]	Δ IVD 2) [mg/valve]
Comp. 9	-	-	325	304
Comp. 10	1000	NH <sub>3</sub>	325	5
Inv. 13	1000	DMA 3)	325	3

- 1) Number average molecular weight of polyisobut enyl radical  
**10** 2) IVD = intake valve deposits; mean of deposits on all valves  
 3) Dimethylamine

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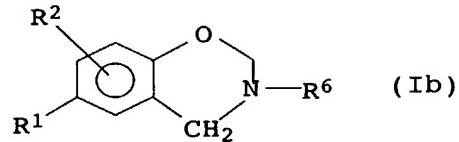
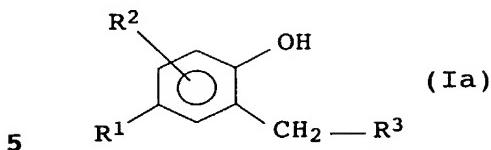
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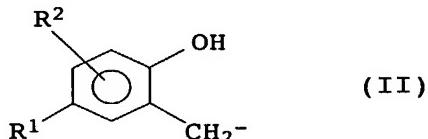
We claim:

1. A process for the preparation of  
5 polyisobutenyphenol-containing Mannich adducts by
  - a) alkylation of a phenol with polyisobutene having more than 70 mol % of vinylidene double bonds and a number average molecular weight of from 300 to 3000 at below  
10 about 50°C in the presence of an alkylation catalyst;
  - b) reaction of the reaction product from a) with  
15 formaldehyde, an oligomer or a polymer of formaldehyde and  
at least one amine which has at least one secondary amino function and no primary amino function  
or  
20
  - c) reaction of the reaction product from a) with at least one adduct of at least one amine which has at least one secondary or primary amino function and formaldehyde, an oligomer of formaldehyde, a polymer of formaldehyde or a  
25 formaldehyde equivalent.
2. A process as claimed in claim 1, wherein the amine used is  
3-(dimethylamino)-n-propylamine,  
di[3-(dimethylamino)-n-propyl]amine, dimethylamine,  
30 diethylamine, di-n-propylamine or morpholine.
3. A process as claimed in claim 1, wherein, in step c), the adduct used is an aminal of formaldehyde with a secondary amine, selected from di-C<sub>1</sub>-C<sub>8</sub>-alkylamines whose alkyl groups  
35 may be substituted by an N(C<sub>1</sub>-C<sub>4</sub>-alkyl)<sub>2</sub> group, and cyclic amines, which have 4 to 6 carbon atoms and whose cyclic structure may be interrupted by O and/or N-C<sub>1</sub>-C<sub>4</sub>-alkyl.
4. A process as claimed in any of the preceding claims, wherein  
40 an adduct mixture is obtained which comprises at least 40 mol% of compounds of the formula Ia and/or Ib,



where

- 10      R<sup>1</sup> is a terminally bonded polyisobut enyl radical,  
 R<sup>2</sup> is H, C<sub>1</sub>- to C<sub>20</sub>-alkyl, C<sub>1</sub>- to C<sub>20</sub>-alkoxy, hydroxyl,  
       a polyalkylenyl radical or CH<sub>2</sub>NR<sup>4</sup>R<sup>5</sup>, where R<sup>4</sup> and R<sup>5</sup> have  
       the meanings stated below, and  
 R<sup>3</sup> is NR<sup>4</sup>R<sup>5</sup>, where R<sup>4</sup> and R<sup>5</sup>, independently of one another,  
       are selected from H, C<sub>1</sub>- to C<sub>20</sub>-alkyl, C<sub>3</sub>- to  
       C<sub>8</sub>-cycloalkyl and C<sub>1</sub>- to C<sub>20</sub>-alkoxy radicals which may be  
       interrupted and/or substituted by heteroatoms selected  
       from N and O, and phenol radicals of the formula II



where R<sup>1</sup> and R<sup>2</sup> are as defined above;  
 with the proviso that R<sup>4</sup> and R<sup>5</sup> are not simultaneously H or phenol radicals of the formula II; or R<sup>4</sup> and R<sup>5</sup>, together with the N atom to which they are bonded, form a 5-, 6- or 7-membered cyclic structure which has one or two heteroatoms selected from N and O and may be substituted by one, two or three C<sub>1</sub>- to C<sub>6</sub>-alkyl radicals; and  
 is a radical R<sup>4</sup> or R<sup>5</sup> other than H.

- 35 5. A process as claimed in any of the preceding claims, wherein  
a Mannich adduct having a polydispersity of from 1.1 to 3.5  
is obtained.

40 6. A process as claimed in any of the preceding claims, wherein,  
in step c), an adduct which is obtained from at least one  
amine and formaldehyde, an oligomer of formaldehyde, a  
polymer of formaldehyde or a formaldehyde equivalent by  
reacting the two reactants for at least 15 minutes at above  
+15°C is used.

45 7. A process as claimed in any of claims 1 to 6, wherein the  
reaction mixture from b) or c) is fractionated by column  
chromatography over an acidic stationary phase by multistage  
elution with

- at least one hydrocarbon and then
- at least one basic alcohol/water mixture.

8. A process as claimed in claim 7, wherein the basic  
5 alcohol/water mixture used is a mixture of

- a) from 75 to 99.5% by weight of at least one C<sub>2</sub>- to C<sub>4</sub>-alcohol,
- b) from 0.4 to 24.4% by weight of water and
- 10 c) from 0.1 to 15% by weight of at least one amine which is volatile at room temperature.

9. A process as claimed in any of the preceding claims, wherein  
the adduct mixture obtained includes from 0 to 20, preferably  
15 1 to 15, mol% of polyisobutenyphenols from reaction step a)  
which are not reacted further.

10. A Mannich adduct obtainable by

- 20 a) alkylation of a phenol with polyisobutene having more than 70 mol % of vinylidene double bonds and a number average molecular weight of from 300 to 3000 at below about 50°C in the presence of an alkylation catalyst;
- 25 b) reaction of the reaction product from a) with formaldehyde, an oligomer or a polymer of formaldehyde and at least one amine which has at least one secondary amino function and no primary amino function.

30 11. The use of a Mannich adduct as claimed in claim 10 as a detergent additive in fuel and lubricant compositions.

12. An additive concentrate containing, in addition to conventional additive components, at least one Mannich adduct  
35 as claimed in claim 10 in amounts of from 0.1 to 99.9% by weight, preferably 0.5 to 80% by weight.

13. A fuel composition containing a main amount of a liquid hydrocarbon fuel and an amount, having detergent activity, of  
40 at least one adduct as claimed in claim 10.

14. A lubricant composition containing a main amount of a liquid, semisolid or solid lubricant and an amount, having detergent activity, of at least one adduct as claimed in claim 10.

**Amended pages annexed to the IPER**

43a

15. The use of a fuel composition as claimed in claim 13 as a gasoline or diesel fuel

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**Preparation of polyisobutenyphenol-containing Mannich adducts****5 Abstract**

Polyisobutenyphenol-containing Mannich adducts are prepared by

- a) alkylation of a phenol with highly reactive polyisobutene at 10 below about 50°C in the presence of an alkylation catalyst;
- b) reaction of the reaction product from a) with formaldehyde, an oligomer or a polymer of formaldehyde and 15 at least one amine which has at least one secondary amino function and no primary amino function,  
or
- c) reaction of the reaction product from a) with at least one adduct of at least one amine which has at least one secondary or primary amino function and formaldehyde, an oligomer of formaldehyde, a polymer of formaldehyde or a formaldehyde equivalent,  
25 and are used as detergent additives in fuel and lubricant compositions, and additive concentrates, fuel compositions and lubricant compositions contain these Mannich adducts.

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(12) NACH DEM VERTRAG ÜBER DIE INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES  
PATENTWESENS (PCT) VERÖFFENTLICHTE INTERNATIONALE ANMELDUNG

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(51) Internationale Patentklassifikation<sup>7</sup>: C08F 8/32, C10L 1/22, C10M 159/16 (74) Anwälte: KINZEBACH, Werner usw.; Ludwigsplatz 4, 67059 Ludwigshafen (DE).

(21) Internationales Aktenzeichen: PCT/EP00/09746

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Veröffentlicht:

- Mit internationalem Recherchenbericht.
- Vor Ablauf der für Änderungen der Ansprüche geltenden Frist; Veröffentlichung wird wiederholt, falls Änderungen eintreffen.

Zur Erklärung der Zweibuchstaben-Codes, und der anderen Abkürzungen wird auf die Erklärungen ("Guidance Notes on Codes and Abbreviations") am Anfang jeder regulären Ausgabe der PCT-Gazette verwiesen.

(54) Title: METHOD FOR PRODUCING MANNICH ADDUCTS THAT CONTAIN POLYISOBUTYLENE PHENOL

(54) Bezeichnung: VERFAHREN ZUR HERSTELLUNG POLYISOBUTENPHENOL-HALTIGER MANNICHADDUKTE

(57) Abstract: The invention relates to a method for producing Mannich adducts that contain polyisobutylene phenol by: a) alkylating a phenol with highly-reactive polyisobutylene at a temperature lower than approximately 50 °C and in the presence of an alkylation catalyst; b) reacting the reaction product from a) with formaldehyde, an oligomer or with a polymer of the formaldehyde and with at least one amine, which has at least one secondary amino function and does not have any primary amino function; or c) reacting the reaction product from a) with at least one adduct consisting of at least one amine, which has at least one secondary or primary amino function, and with formaldehyde, an oligomer of the formaldehyde, a polymer of the formaldehyde or with a formaldehyde equivalent. The invention also relates to Mannich adducts that can be obtained by using this method, to the use of the Mannich adducts as detergent additives in fuel compositions and lubricant compositions, and to additive concentrates, fuel compositions and lubricant compositions containing these Mannich adducts.

(57) Zusammenfassung: Gegenstand der vorliegenden Erfindung ist ein Verfahren zur Herstellung Polyisobutenphenol-haltiger Mannichaddukte durch: a) Alkylierung eines Phenols mit hochreaktivem Polyisobuten bei einer Temperatur unterhalb von etwa 50 °C in Gegenwart eines Alkylierungskatalysators; b) Umsetzung des Reaktionsproduktes aus a) mit Formaldehyd, einem Oligomer oder einem Polymer des Formaldehyds und wenigstens einem Amin, das wenigstens eine sekundäre Aminofunktion und keine primäre Aminofunktion aufweist; oder c) Umsetzung des Reaktionsproduktes aus a) mit wenigstens einem Addukt aus wenigstens einem Amin, das wenigstens eine sekundäre oder primäre Aminofunktion aufweist, und Formaldehyd, einem Oligomer des Formaldehyds, einem Polymer des Formaldehyds oder einem Formaldehydäquivalent, die nach diesem Verfahren erhältlichen Mannichaddukte, die Verwendung der Mannichaddukte als Detergentsadditive in Kraft- und Schmierstoffzusammensetzungen, sowie Additiv-Konzentrate, Kraftstoffzusammensetzungen und Schmierstoffzusammensetzungen, die diese Mannichaddukte enthalten.

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# Declaration, Power of Attorney

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0050/050788

We (I), the undersigned inventor(s), hereby declare(s) that:

My residence, post office address and citizenship are as stated below next to my name,

We (I) believe that we are (I am) the original, first, and joint (sole) inventor(s) of the subject matter which is claimed and for which a patent is sought on the invention entitled

**Method for producing Mannich adducts that contain polyisobutylene phenol**

the specification of which

[ ] is attached hereto.

[ ] was filed on \_\_\_\_\_ as

Application Serial No. \_\_\_\_\_

and amended on \_\_\_\_\_.

[x] was filed as PCT international application

Number PCT/EP00/09746

on 5 October 2000

and was amended under PCT Article 19

on \_\_\_\_\_ (if applicable).

We (I) hereby state that we (I) have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

We (I) acknowledge the duty to disclose information known to be material to the patentability of this application as defined in Section 1.56 of Title 37 Code of Federal Regulations.

We (I) hereby claim foreign priority benefits under 35 U.S.C. § 119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed. Prior Foreign Application(s)

Application No.	Country	Day/Month/Year	Priority Claimed
19948111.3	Germany	06 October 1999	[x] Yes [ ] No

## **Declaration**

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0050/050788

We (I) hereby claim the benefit under Title 35, United States Codes, § 119(e) of any United States provisional application(s) listed below.

(Application Number)

(Filing Date)

(Application Number)

(Filing Date)

We (I) hereby claim the benefit under 35 U.S.C. § 120 of any United States application(s), or § 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. § 112, I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR § 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.

**Application Serial No.**

**Filing Date**

**Status (pending, patented,  
abandoned)**

And we (I) hereby appoint:

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Registration Number 31, 451;  
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Registration Number 32, 884;  
Registration Number 36, 379;  
Registration Number 33, 893; o

Robert W. Hahl, Registration Number ~~33,893~~, our (my) attorneys, with full powers of substitution and revocation, to prosecute this application and to transact all business in the Patent Office connected therewith; and we (I) hereby request that all correspondence regarding this application be sent to the firm of **OBLON, SPIVAK, McCLELLAND, MAIER & NEUSTADT, P. C.**, whose Post Office Address is: Fourth Floor, 1755 Jefferson Davis Highway, Arlington, Virginia 22202.

We (I) declare that all statements made herein of our (my) own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

**Declaration**

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## **Declaration**

Page 4 of 4

0050/050788

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